Kinetic parameters of thermal destruction of the copolymer of polyethylene glycol fumarate with acrylic acid in inert medium

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Thermal decomposition of the copolymer of polyethylene glycol fumarate with acrylic acid (p-EGF:AA) of two different compositions synthesized earlier was studied in the present work. TG and DTG curves prove that decomposition takes place in several stages. According to thermogravimetric curves it has been found out that for the copolymer with higher content of acrylic acid the decomposition of the copolymer's sample is started at higher temperatures. It has been shown the shift of the temperature of decomposition's start to the higher area with the increase of heating rate which is necessary for the detorsion of macromolecular coil. Experimental data processed using graphical methods of Kissinger–Akahira–Sunose and Friedman allowed us to calculate the activation energy of the thermal decomposition process. It has been established that the copolymer with the composition of 21.03:78.97 mass.% has lower meaning of activation energy than the one with the composition of 68.96:31.04 mass.%. As a result of calculation one can see that the meanings found out using these methods depend slightly on conversion. Using Achar-Brindley-Sharp method and the method of invariant kinetic parameters the kinetic triplet of the decomposition process has been found which was used to build the calculated curve. The dependences of g(α) on α using these parameters showed a satisfactory agreement of calculated curves with the experimental ones. One can conclude that the decomposition process of the copolymer of polyethylene glycol fumarate with acrylic acid is well described with of D3 (three-dimensional diffusion) model.

Keywords: thermogravimetry; activation energy; copolymers; polyethylene glycol fumarate; acrylic acid.

Инертті ортада акрил қышқылымен полиэтиленгликолумарат сополимерінің термиялық деструкциясының кинетикалық параметрлері

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Бұл жұмыста бұрын синтезделген екі түрлі құрамдағы акрил қышқылымен полиэтиленгликольфумарат сополимерінің (п-ЭГФ:АҚ) термиялық ыдырауы зерттелген. TG және DTG қисықтары ыдырау процесі бірнеше сатыда жүретінін дәлелдейді. Термогравиметриялық қисық сызыққа сәйкес, құрамында акрил қышқылы көп сополимер үшін сополимер үлгісінің ыдырауы жоғары температурада басталатыны анықталды. Макромолекулалық шарларды айналдыру қажеттілігімен байланысты қыздыру жылдамдығының жоғарылауымен жоғары аймаққа ыдыраудың басталу температурасының өзгеруі көрсетілген. Фридман мен Киссинджер-Акахир-Сануздын графикалық әдістерімен өңделген эксперименттік мәліметтер термиялық ыдырау процесінің активтену энергиясын есептеуге мүмкіндік берді. 21.03:78.97 масс. % құрамының сополимері 68.96:31.04 масс. % -тен жоғары ыдырау активтендіру энергиясына ие екендігі анықталды. Есептеулер нәтижелері бойынша осы әдістермен табылған мәндер конверсияға қатты тәуелді емес екенін көруге болады. Ахар-Бриндли-Шарпа әдісін және инвариантты кинетикалық параметрлер әдісін қолдана отырып, есептелген қисық сызықты құру үшін қолданылатын ыдырау процесінің кинетикалық триплеті табылды. Осы параметрлерді қолдана отырып, g(α) α-ға тәуелділігі есептеу қисықтарының тәжірибелік қисықтармен қанағаттанарлық келісімін көрсетті. Акрил қышқылымен полиэтиленгликольфумарат сополимерінің ыдырау процесі D3 (үш өлшемді диффузия) моделімен жақсы сипатталған деп айта аламыз.

Түйін сөздер: термогравиметрия; активтендіру энергиясы; сополимерлер; полиэтиленгликольфумарат; акрил қышқылы.

Кинетические параметры термической деструкции сополимера полиэтиленгликольфумарата с акриловой кислотой в инертной среде

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В настоящей работе исследовано термическое разложение синтезированного ранее сополимера полиэтиленгликольфумарата с акриловой кислотой (п-ЭГФ:АК) двух различных составов. TG и DTG кривые доказывают, что процесс разложения происходит в несколько стадий. По термогравиметрическим кривым установлено, что для сополимера с большим содержанием акриловой кислоты разложение образца сополимера начинается при более высоких температурах. Показан сдвиг температуры начала разложения в более высокую область с ростом скорости нагрева, связанный с необходимостью раскручивания макромолекулярных клубков. Экспериментальные данные, обработанные графическими методами Фридмана и Киссинджера-Акахира-Сануза, позволили рассчитать энергии активации процесса термического разложения. Установлено, что сополимер с составом 21.03:78.97 масс. % имеет энергию активации разложения выше, чем 68.96:31.04 масс. %. По результатам расчетов можно увидеть, что значения, найденные данными методами, не сильно зависят от конверсии. Используя метод Ахара-Бриндли-Шарпа и метод инвариантных кинетических параметров, найден кинетический триплет процесса разложения, который использован для построения расчетной кривой. Зависимости g(α) от α с использованием данных параметров показали удовлетворительное согласие расчётных кривых с экспериментальными. Можно сказать, что процесс разложения сополимера полиэтиленгликольфумарата с акриловой кислотой хорошо описывается моделью D3 (трехмерная диффузия).

Ключевые слова: термогравиметрия; энергия активации; сополимеры; полиэтиленгликольфумарат; акриловая кислота.

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1. Introduction

The study of the kinetics of thermal decomposition of the copolymers on the basis of unsaturated polyester resins is of great importance from the scientific point of view within the last decades as the study of physicochemical properties of such objects has vital role in modern industry [1].

Unsaturated polyesters are obtained by condensation polymerization of unsaturated dicarbon acids or their mixtures with saturated acids with polyhydric alcohols [2]. Compositional materials based on polyester resins have wide application as binding, film-forming, impregnated and filling compounds [3]. Besides, the ease of processing the unsaturated polyesters to the end-product makes actual the use of the copolymers on their basis for the number of industrial directions and therefore the question of the level of their thermal stability is of special importance [4,5].

Usually the thermogravimetry is used for the study of thermal destruction of polymers. Qualitative analysis of experimental data depends on reliable estimation of kinetic parameters $E_{a,}$ A and f(a), and in essence it gives mathematical explanation which is necessary for the extrapolation of the behavior of the decomposition reaction. In this regard there were worked out many different methods for the determination of kinetic parameters on the basis of experimental data of thermogravimetry [6,7].

At the beginning stage of the studies the main kinetic and thermodynamic parameters of decomposition of some copolymers on the basis of polyethylene glycol fumarate with acrylic acid have been determined with the help of differential and integral methods [8,9]. It was found that at different degrees of conversion, the activation energies are very close: E = 205-227 kJ/mol. And the copolymer is more thermally stable in a nitrogen atmosphere in accordance with the kinetic parameters. The result of the study has shown the practical value of this procedure.

The aim of this work is to make a comparative analysis of the kinetics of thermal decomposition of the samples of polyethylene glycol fumarate with acrylic acid of the composition of 21.03:78.97 and 68.96:31.04 mass.%.

2. Experiment

Study of thermal properties of p-EGF:AA copolymer in three parallel experiments was made with the help of device for simultaneous thermal analysis Labsys Evolution TG-DTA/DSC of «Setaram» brand in dynamic mode with temperature range of 30-600°C at heating in Al_2O_3 crucible with rate of 2.5, 5, 10 and 20°C/min in nitrogen atmosphere with stream rate of 30 mL/min. Calibration of device for thermogravimetric studies and heat flow rate was carried out three fold under the $CaCO_3$ standards and In respectively.

The kinetics of thermal decomposition is usually expressed by the following equation:

$$\frac{d\alpha}{dt} = k(T) \tag{1}$$

where k is the rate constant, t is the reaction time, α is the conversion, which is described as:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \tag{2}$$

where m_i, m_t, and m_f are the mass at the beginning, at time t, and at the end of the reaction.

The decomposition rate constant (k(T)) is a temperature-dependent function and is usually described by the Arrhenius equation.

Hence, the equation (1) can be written as follows:

$$\frac{d\alpha}{dt} = Aexp\left(\frac{-E}{RT}\right)f(\alpha) \tag{3}$$

where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant (8,314 J·mol^{-1}), *f(α)* is the reaction model and T is the temperature (K).

Integral and differential methods were used to determine the activation energy (E_a).

The **Kissinger–Akahira–Sunose** method [10,11] is based on the following expression:

$$ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = Const - \left(\frac{E}{RT}\right) \tag{4}$$

where β_i is the heating rate (°C/min).

The activation energy can be obtained from a plot of $ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ versus 1/T, for a given value of the degree of conversion, α, where the slope is equal to E_a /R.

The most common differential isoconversion method is that **Friedman** method [12]. The method is based on the equation:

$$ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = ln[f(\alpha)A_\alpha] - \frac{E_a}{RT_{\alpha,i}} \tag{5}$$

Eq. (5) is applicable to any temperature program. At each given a the value of E_a is determined from the slope of a plot of $ln(\beta_i{*}d\alpha/dt)_{\alpha,i}$ against $1/T_{\alpha,i}$. The index is introduced to denote various temperature programs.

To define the reaction model and pre-exponential factor, method of invariant kinetic parameters and model fitting method were used in this work. Differential method of Achar-Brindley-Sharp [13] was obtained as the result of equation logarithm (3):

$$ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = lnA - \frac{E}{RT} \tag{6}$$

Left part of equation (6) for this analytic form *f(α)* will be straight line, whose incline and crossing allow the estimation of activation energy and pre-exponential factor, respectively. Despite the fact that parameters are modified in wide range with *f(α)*, they all demonstrate the strong correlation, known as compensation effect:

$$lnA_i = a^*E_i + b^* \tag{7}$$

where a^* and b^* are the compensation parameters and the subscript i refers to a factor producing a change in the Arrhenius parameters(conversion, temperature program).

Using the ratio of apparent compensation effect, compensation parameters are defined for each heating rate. Thus, diagram a^* *vs* b^* represents the straight line, whose parameters allow estimating the invariant kinetic parameters [6]:

$$b^* = lnA + a^*E \tag{8}$$

3. Results and Discussion

At practical application of polymers, thermal stability in necessary temperature range plays a great role. Copolymers of unsaturated polyether resins with hydrophobial monomers, having the spatial linked structure, are distinct with thermal stability in wide range of temperatures and are widely described in the literature [14,15]. In the result of studies it was found that composition of unsaturated polyether and monomers used for linking influences significantly the thermal stability of copolymerization products, presence of aliphatic inclusions in copolymer decreases the thermal resistance. Increase of degree of unsaturation of polyether resin, as well as increase of polyether resin content compared to monomer leads to increase of thermal stability of copolymers. Results of thermogravimetric analysis showed that these copolymers are thermally resistant up to 250-300°C, and after this thermal destruction happens, that runs in several steps.

At the first time synthesized copolymers of polyglycolemaleanates with unsaturated carbonic acids have spatial linked structure as well [16,17], and it seemed interesting to study the influence of temperature on their behavior by thermogravimetry. In this work, is a previously synthesized copolymers p-EGF:AA of composition 21.03:78.97 and 68.96:31.04 mass.% is the object of research [18], which have proven themselves as «smart» systems. Thermogravimetric analysis was performed in dynamic conditions at four different heating rates. Figure 1a shows the dependence of sample weight from the temperature, and figure 1b shows the curves of the rate of decomposition.

As we see in Figure 1a, increase in the composition of acrylic acid leads to the offset of copolymer decomposition start to the area of higher temperatures. This concept is illustrated slower with DTG curve (Figure 1b): thus, maximum rate of copolymer decomposition is moved from 356 to 375ºC. Figure 1 shows that decomposition process is started at the temperature of ~150°C, and then there is step-by-step decreasing of sample weight with emission of volatile matters. The second stage of decomposition starts at the temperature of 265°C and is finished at 480°C, with a lower ratio of acrylic acid. With a ratio of 21.03:78.97 mass.%, start and final decomposition temperature moved to 280 and 500°C respectively. The same trend is observed in DTG curve. Residue weight at the end amounts approximately 15-17 percent of total sample weight.

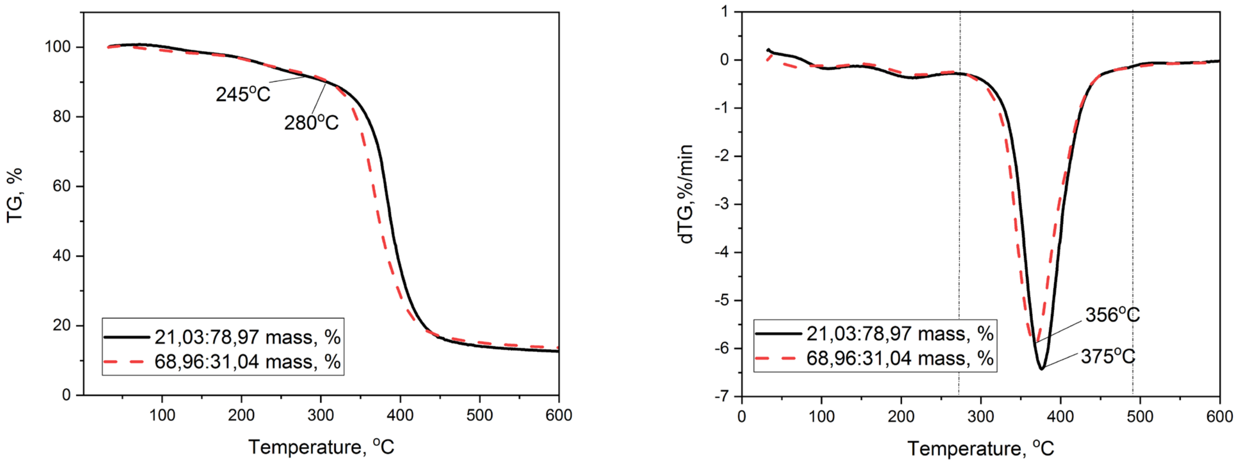

Figure 1 – TG (a) and DTG (b) curves of p-EGF:AA 21.03:78.97 and 68.96:31.04 mass.% at heating rate 5°C/min

To process the thermogravimetric curves at different heating rates, areas with highest weight loss are selected. Figure 2 shows the dependence of conversion degree and temperature.

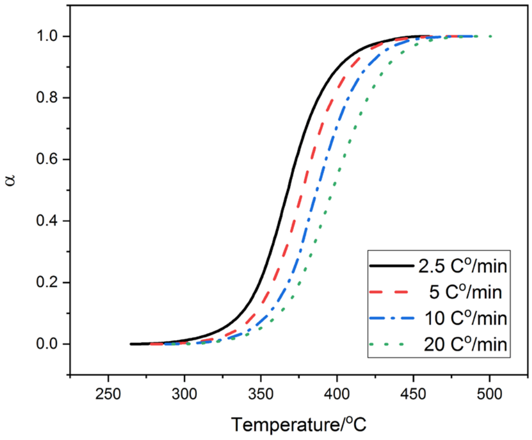

Figure 2 – Dependence of the conversion (α) of the copolymer p-EGF:AA 21.03:78.97 mass.% on the temperature at different heating rates

With the aim to estimate the thermodynamic stability subject to activation energy of copolymers, equations the Kissinger–Akahira–Sunose and the Friedman was applied. Selection of these methods was conditioned with the possibility to compare the activation energies obtained by integral and differential methods, which allow to estimate the legitimacy of allowances made at equation derivation. Dependence diagrams of equations are shown in the Figure 3 a, b, c and d.

As can be seen from the graphs, the points obtained by the Friedman differential method have a greater scatter (Figure 3) than in the Kissinger-Akahira-Sunose (KAS) method, and as a consequence, the latter are more parallel to each other. For all the obtained partial dependencies, activation parameters are calculated; their values are shown in Table 1.

As we see in Table 1, activation energies at different levels of conversion, have good convergence for both methods. At the primary stage of decomposition, activation energy values are changed in the range ~236 and 271 kJ/mol. Further we can observe stabilization and slight decrease. At value of α > 0.7 activation energy starts increasing gradually and reaches its maximum at α = 0.9. Increase of E_a is mainly connected to intensive decomposition of copolymer p-EGF:AA at high temperatures in inert media. As well, high values of activation energy in the beginning of the process witness the complex processes, happened at thermal destruction, related to breaking of unsaturated double bonds in copolymer structure.

Using equation 6, thirteen values of E_i and $\ln A_i$ were obtained for respective reaction models. Since for invariant kinetic parameters method it is necessary for E_a not to depend strongly on level of transformation, the range 0.1-0.9 was selected.

Figure 4a shows that for the ratio 21.03:78.97, the points lie on the same straight line and have a high degree of correlation, and for the ratio 68.96:31.04, the degree of correlation is slightly lower (Figure 4b). In inclination and crossing of the diagram, invariant kinetic parameters of copolymer decomposition were found, E_a = 240 kJ/mol and lnA = 38 for a copolymer with a lower ratio of polyester resin and E_a = 248 kJ/mol and lnA = 40 with a higher ratio. Activation energy conforms with values obtained by isoconversion methods.

When both parameters are defined, we can numerically reconstruct the reaction models in any integral or differential

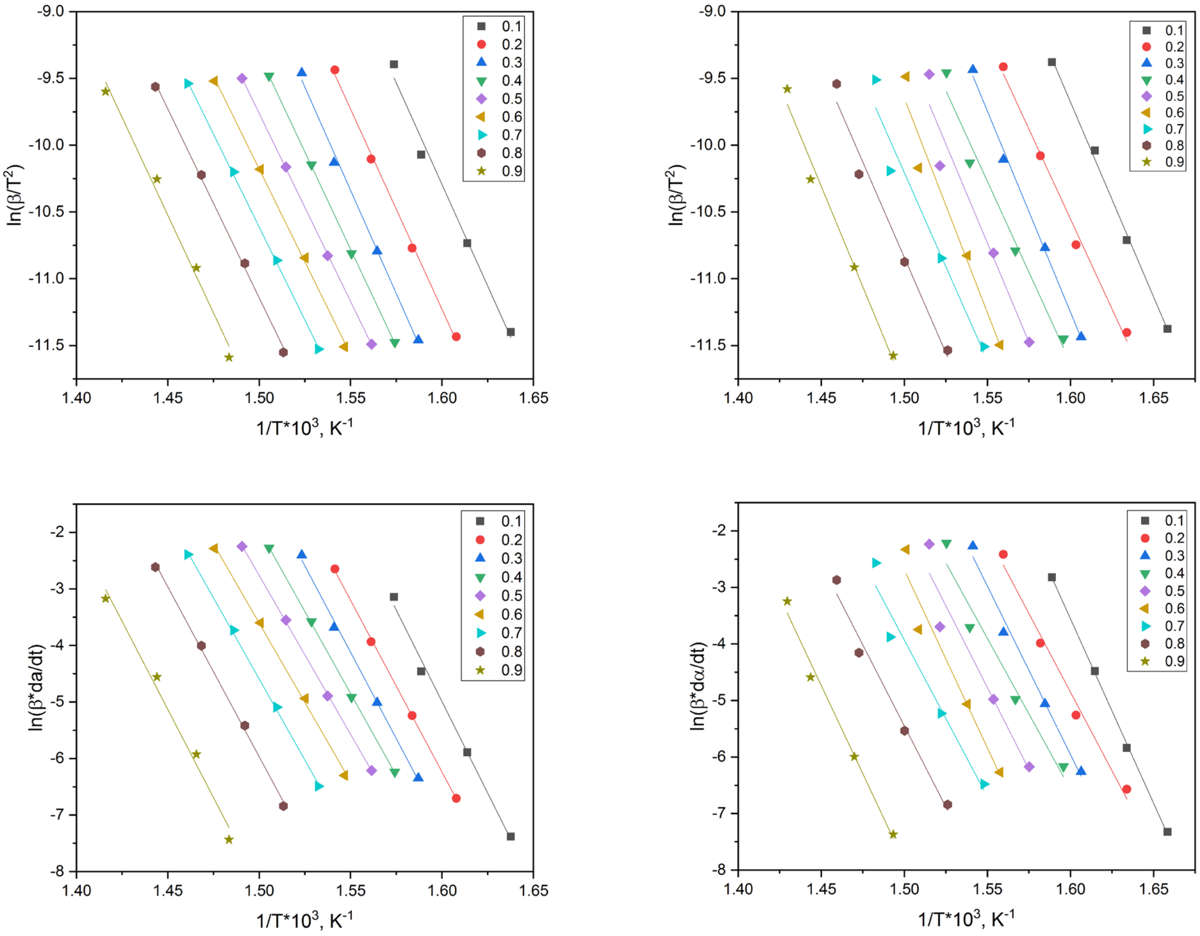

Figure 3 – Kissinger-Akahira-Sunose (a,b) and Friedman (c,d) plots of p-EGF:AA 21.03:78.97 and 68.96:31.04 mass.%

Table 1 – Kinetic parameters according to, Kissinger-Akahira-Sunose and Friedman

α, %	Kissinger-Akahira-Sunose				Friedman			
	21.03:78.97		68.96:31.04		21.03:78.97		68.96:31.04	
	E_a, kJ/mol	R^2	E_a, kJ/mol	R^2	E_a, kJ/mol	R^2	E_a, kJ/mol	R^2
0.1	236.21	0.9881	242.51	0.9967	248.26	0.9936	271.19	0.9993
0.2	232.57	0.9979	223.95	0.9919	244.16	0.9996	231.25	0.9859
0.3	240.42	0.9961	250.39	0.9966	237.38	0.9975	247.91	0.9885
0.4	233.72	0.9998	226.02	0.9766	232.53	0.9997	222.04	0.9608
0.5	225.87	0.9999	246.61	0.9438	225.28	0.9997	240.61	0.9303
0.6	222.79	0.9986	267.16	0.9555	224.76	0.9981	261.84	0.9486
0.7	223.12	0.9995	234.02	0.9558	230.13	0.9990	230.68	0.9582
0.8	226.84	0.9983	237.56	0.9790	237.48	0.9980	238.34	0.9829
0.9	235.11	0.9884	250.03	0.9849	242.70	0.9853	259.55	0.9880
Mean	**230.74**	**0.9963**	**242.03**	**0.9756**	**235.85**	**0.9967**	**244.82**	**0.9714**

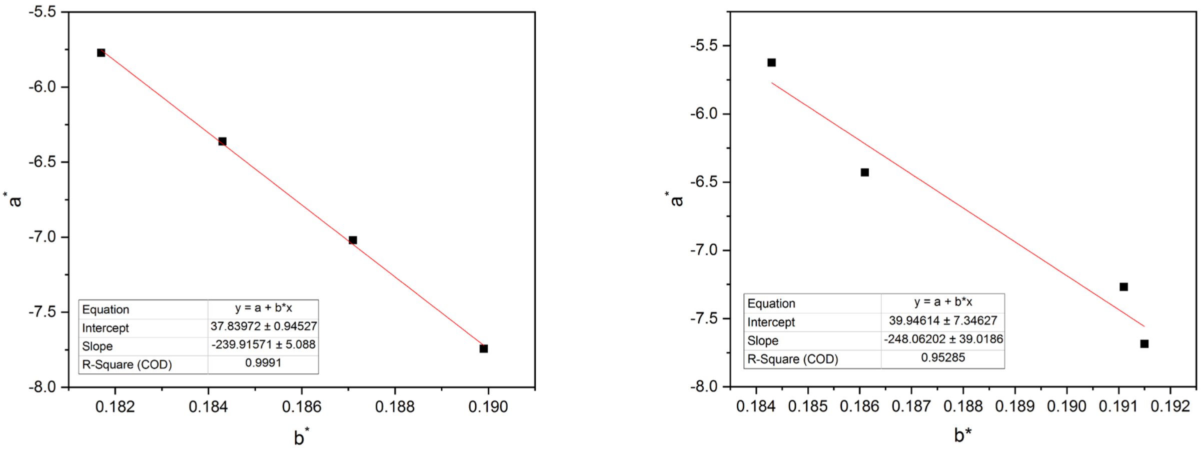

Figure 4 – Plot of the supercorrelation ratio (a* vs b*) of p-EGF:AA 21.03:78.97 mass.% (a) and 68.96:31.04 mass.% (b)

Table 2 – Some of the kinetic models used in the solid-state kinetics

#	Reaction model	Code	*f(α)*	*g(α)*
1	Power law	P4	$4\ \alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	P3	$3\ \alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	P2	$2\ \alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	P2/3	$2/3\ \alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion Mampel (first	D1	$1/2\ \alpha^{-1}$	α^{2}
6	order)	F1	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion Contracting	D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)]^{1/3}]^{-1}$	$[1-(1-\alpha)]^{1/3}]^{2}$
11	sphere	R3	$3(1-\alpha)$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	R2	$2(1-\alpha)$	$1-(1-\alpha)^{1/2}$
13	Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$

form. The models used in this study have been summarized in Table 2. Integral form might be reconstructed by value substitution of E_a and A to the equation [19]:

$$g(\alpha) = \frac{A}{\beta}\int_0^{T_\alpha} exp\left(\frac{-E}{RT}\right) dT \qquad (9)$$

With the help of equation 9, the set of numeric values g(α) for different conversion levels was obtained. With the aim to check the correctness of obtained data, we made the attempt to compare the experimental curves with calculated ones.

The dependence graph of the reaction model on the conversion degree has a profile reminiscent of an accelerating reaction (F1, D1, R3, etc.). Therefore, the calculated data were compared to the previously selected theoretical graphs g(α). As seen in Figure 8, a good conformity was found for the D3 model, the same situation is peculiar for other values of heating rate.

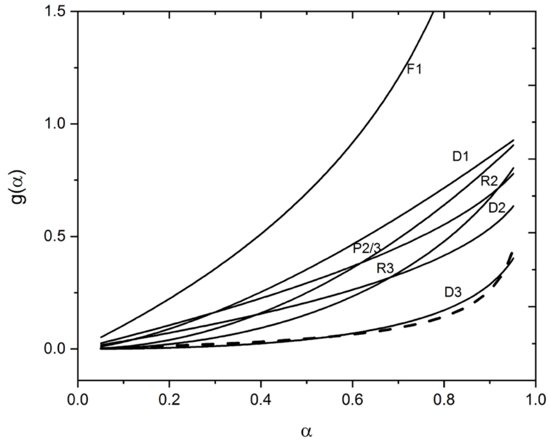

Figure 5 – Theoretical g(α) plots as a function of conversion a for several kinetic models and experimental plot for kinetic model D3 (dotted lines)

4. Conclusion

Thermal decomposition of copolymer p-EGF:AA at different heating rates was studied, and it showed that growth of the latter moves the decomposition start temperature to higher area. Comparative analysis showed that the more heat-resistant is that the copolymer with a lower content of polyester resin. Activation parameters of decomposition reaction are calculated with isoconversion methods of Friedman and Kissinger-Akahira-Sunose, which have high converging.

Combining different methods, kinetic triplet was obtained, corresponding to $E_a \approx 240$ kJ/mol, $A \approx 3{,}19 \cdot 10^{16}$ min^{-1} for a copolymer of composition 21.03:78.97 mass.% and $E_a \approx 248$ kJ/mol, $A \approx 2{,}35 \cdot 10^{17}$ min^{-1} for a copolymer of composition 68.96:31.04 mass.%. Using the integrated Arrhenius equation, calculated curves of thermogravimetric analysis are composed, which have slight divergence with experimental ones. Thus, we may say that p-EGF:AA copolymer decomposition processes fully described with D3 model $g(\alpha) = [1-(1-\alpha)]^{1/3}]^2$.

Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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