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Comparative Analysis of Thermal Decomposition Kinetics of Copolymers Based on Polyethylene Glycol Fumarate with Methacrylic Acid

The thermal properties of a copolymer based on polyethylene glycol fumarate with methacrylic acid in a nitrogen atmosphere were studied in this paper. Four various heating rates and two types of a polyester resin composition were used. The analysis of thermal decomposition kinetics was implemented. Three kinetics methods namely Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Friedman were applied. Curves of a thermogravimetric analysis demonstrated that the thermal decomposition of copolymers with different molar ratios was observed. It was determined that the kinetic data depends on the studied copolymers' composition. The obtained data showed a good convergence in various heating rates. Also, the thermodynamic characteristics were calculated namely the changes in the Gibbs energy (ΔG), enthalpy (ΔH) and entropy of activation (ΔS). The Achar-Brindley-Sharp method was used to find the invariant kinetic parameters of decomposition. Thus, the the kinetic compensation effect was applied to define a reaction model and a pre-exponential factor. A main phase of the copolymer decomposition in a narrow temperature range was determined. It was attested by a peak on the differential curve. An insignificant mass loss of the volatile-matter yield was observed in the range of 30–150 °C.

Keywords: dynamic thermogravimetry, thermal decomposition, copolymer based on polyethylene glycol fumarate with methacrylic acid, activation energy, isoconversional kinetic analysis.

Introduction

Hydrogels are the promising materials to use in the practice. They have some special physicochemical properties such as high susceptibility and sensitivity to environmental changes and shape variability [1]. The spread spectrum to use hydrogels was intensified the search for the new monomers to synthesize such polymers [2–5]. The unsaturated polyester resins are of a particular interest to obtain the above mentioned materials.

It's a well-known fact that the unsaturated polyester resins have a complex of the useful properties such as lower viscosity and efficient curing by vinyl monomers in comparison with the epoxy resins. As a result, it demonstrates their higher reactivity [6].

Despite the aforementioned advantages of the unsaturated polyesters, their reactions have not been sufficiently studied. For instance, the literature has some comprehensive data on copolymerization of the unsaturated polyester resins with the hydrophobic monomers [7–9]. However, there is almost no information on their copolymerization with the ionogenic monomers.

In addition, the ionogenic hydrophilic monomers were applied as comonomers of the unsaturated polyester resins to obtain spatially crosslinked polymers with a charged network and high sorption properties [10].

As is known the copolymers of the unsaturated polyester resins have the practical importance, but a limited number of papers on their thermal stability are observed in the literature [11]. The thermal stability with using the thermo-gravimetric analysis in nitrogen to determine the thermal and thermo-oxidative mechanisms was examined in this paper. Also the activation energy was calculated with using the various heating rates. The papers of [12–13] investigated the features of the decomposition kinetics of some unsaturated polyester resin derivatives with an acrylic acid. It was known that a thermal stability of a copolymer based on the unsaturated polyester resins with a methacrylic acid was previously researched at the initial ratios of M1:M2 (wt%) — 6.65:93.35 wt% (under nitrogen atmosphere) [14].

In continuation of the aforementioned investigations, it was interesting to estimate the impact of a temperature factor on stability of the polyethylene glycol fumarate with methacrylic acid with using the dynamic thermogravimetry methods.

Experimental

The previously synthesized [15] copolymers based on polyethylene glycol fumarate (p-EGF) with methacrylic acid (MAA) (6.65:93.35 mol.% and 89.98:10.02 mol.%) were used as subjects of this study. The thermal properties of copolymers (p-EGF:MAA) were studied on Setaram Labsys Evolution TG-DTA/DSC for the synchronous thermal analysis. A dynamic mode, a temperature range of 30-700ºC, heating in Al_2O_3 crucible at a rate of 2.5, 5, 10, 20 °C/min, inert atmosphere with a nitrogen flow rate of 30 ml/min were applied. The device was calibrated for the thermogravimetric studies and heat flow in compliance with standards of $CaCO_3$. The experimental data was processed with using the Microsoft Excel and Processing programs.

Flynn-Wall-Ozawa's integral method

The Flynn-Wall-Ozawa method [16–17], which uses the Doyle's approximation [18], is based on an equation:

$$\ln\left(\beta_i\right) = \text{Const} - 1.052\left(\frac{E_\alpha}{RT_\alpha}\right). \tag{1}$$

The activation energies for various conversion levels are calculated from a slope of $\ln(\beta_i)$ dependence on $1/T$.

Friedman's differential method

The Friedman's differential method is described by a following equation [19]:

$$\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,\,i}\right] = \ln\left[f\left(\alpha\right)A_\alpha\right] - \frac{E_\alpha}{RT_{\alpha,\,i}}. \tag{2}$$

The linear dependence graphs of $\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,\,i}\right]$ on $1/T$ give the straight lines with different slope angles of E/R. Thus, the activation energies are calculated on their basis.

Kissinger-Akahira-Sunose method

The Kissinger-Akahira-Sunose method, which uses a more accurate Murray and White approximations, is based on an equation [20]:

$$\ln\left(\frac{\beta_i}{T^2_{\alpha,\,i}}\right) = \text{Const} - \frac{E_\alpha}{RT_\alpha}. \tag{3}$$

The data were linearized [21]. As a result, the calculated points for all patterns were placed on the straight lines. The least squares method was used. Their tangent of a slope was corresponded to E/R. Their cut-off section on the ordinate axis was conformed to an effective order of a reaction.

Invariant kinetic parameters method

The so-called "compensation effect" was used for the invariant kinetic parameters method and the model-fitting method. So this compensation effect was found in the experiment at a single heating rate to define a reaction model and a pre-exponential factor. The Achar-Brindley-Sharp method [22] was obtained with a logarithmic equation:

$$\ln\left(\frac{dx/dt}{f(\alpha)}\right) = \ln A - \frac{E}{RT}. \tag{4}$$

The precise definition of the reaction model and pre-exponential factors could be achieved with using the foregoing compensation effect. Thus, the values of E_i and A_i were used to determine parameters. The values of a and b were applied for a compensation effect by equation [23]:

$$\ln A_i = a^* E_i + b^*. \tag{5}$$

Once the parameters were defined, the reaction model can be constructed in any integral or differential form with using the values of E_i and A_i by equation [24]:

$$g(a) = \frac{A}{\beta}\int_0^{T_\alpha} \exp\left(\frac{-E}{RT}\right)dt. \tag{6}$$

Thermodynamic study

The thermodynamic parameter can be calculated from a fundamental expression [25–26].

$$k = \frac{x^{ek_B T}}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{E}{RT}\right), \tag{7}$$

where χ — a transmission coefficient. It is taken to be a unity for monomolecular reactions; k_B — the Boltzmann constant; h — the Planck's constant; e — the Neper number; $\Delta S^{\neq}$ — the change of entropy for the formation of the activated complex from a reagent.

The following expression was obtained with using the pre-exponential factor A from the Arrhenius equation:

$$\mathrm{A} = \frac{x^{ek_B T}}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right). \tag{8}$$

After rearranging an equation (8), the change of entropy of the activated complex can be calculated by the following expression (9):

$$\Delta S^{\neq} = R\left(\ln \mathrm{A} - \ln \frac{x^{ek_B T}}{h}\right). \tag{9}$$

Changes in the Gibbs free energy and enthalpy of the activated complex can be calculated by the well-known thermodynamic equations of (10) and (11):

$$\mathrm{E_A} = \Delta H + RT\ ; \tag{10}$$

$$\Delta G = \Delta H - T\Delta S\ . \tag{11}$$

ΔS, ΔH and ΔG were calculated at a temperature equal to the DTG peak temperature, which corresponded to the fastest decomposition temperature.

Results and Discussion

Practice demonstrated that unsaturated polyethers with a low molecular weight and an unsaturated bond are a good framework for synthesis of the spatially crosslinked highly charged cationic and amphoteric polyelectrolytes to interact with the corresponding monomers [13]. It should be noted that the crosslinked copolymers formation at any ratio of the initial comonomer mixture was obtained by the reaction. In this case, a clear pattern of dependence of the swelling ability on the content of polyester resin was observed. Thus, it was explained by a change in a grid density [27]. Previously, our paper of [28] showed that based on the above an increase in the thermal stability of copolymers with high polyester content should be expected. Therefore, it was interesting to evaluate the thermal stability in a comparison of copolymers based on polyethylene glycol fumarate with methacrylic acid, i.e. they were opposite in a molar composition.

The thermal decomposition of p-EGF–MAA copolymers was studied with a molar composition of 6.65:93.35; 89.98:10.02 mol.%. Thus, the dynamic thermogravimetric analysis in a nitrogen atmosphere at various heating rates in a temperature range of 30–600 °C was used. The kinetic data were processed by the Flynn-Wall-Ozawa, Friedman and Kissinger-Akahira-Sunose methods. They were based on the Arrhenius equation and used in studies of many organic and polymeric materials [29–33].

The resulting curves of the thermogravimetric analysis and decomposition rates are demostrated in Figure 1.

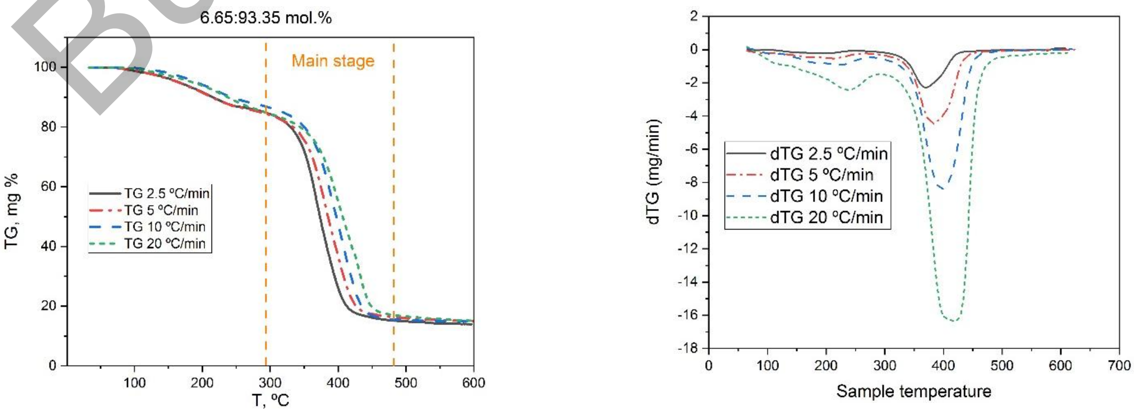


Figure 1. Temperature dependences of the mass change (TG curve), the rate of mass change (DTG) for p-EGF:MAA copolymer at various heating rates, initial ratios (a) of M_1:M_2 in mol. % — 6.65:93.35 mol.%, in a nitrogen atmosphere

Figure 1 demonstrates that transformations were not observed in a substance that lead to a change in its mass on the thermogravimetric curves at 30°C to 100 °C.

An insignificant decomposition of a sample was found for a copolymer with a composition of 6.65:93.35 mol.% at 100–300 °C with yield of some volatile products and mass loss up to ~12%. Further intensive mass loss of the sample with complete process completion at ~500 °C was observed. The total mass loss was ~80 %.

The graph in Figure 2 illustrates that the mass loss was observed noticeably faster with an increase in the heating rate. So the rate of mass loss was low at a heating rate of 2.5°C/min. Thus, the mass loss was found more intensively with an increase in the heating rate.

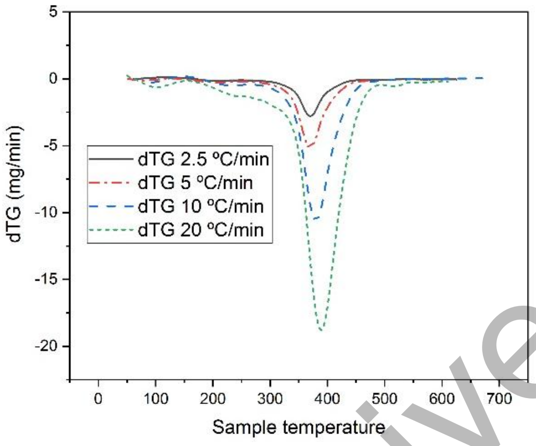


Figure 2. Temperature dependences of the mass change (TG curve), the rate of mass change (DTG) for the p-EGF:MAA copolymer at various heating rates, initial ratios of M_1:M_2 in mol.% — 89.98:10.02 mol.%, in a nitrogen atmosphere

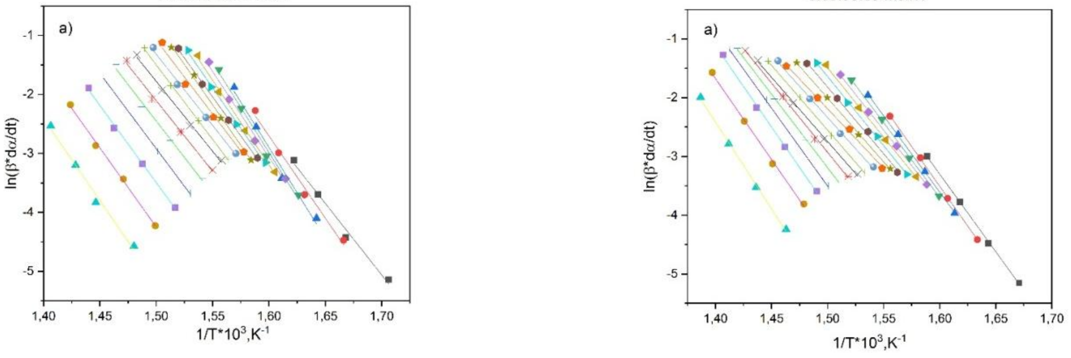
The volatile-matter yield for a copolymer with a high content of polyester resin started at higher temperatures (maximum at 320 °C). The temperature range of 320–500 °C demonstrated the decomposition of a copolymer's basic mass with a total residue of ~15 %. The same rule was also used for the second sample, i.e. its heating speed raised and its mass loss rate has increased.

The comparative analysis of curves of 1 and 2 demonstrated that when a polyester content increased in a copolymer, the decomposition had higher temperatures. As noted above, it was apparently associated with an increase in a grid density.

Kinetic analysis

The isoconversion principle was used to calculate the kinetic parameters. Thus, dependences of parameters of the Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Friedman equations at various transformation degrees were established in Figure 3.

Figure 3 showed the linearization of data for two different copolymers with slight differences, i.e. it depended on the polyester resin content. Based on these differences, the activation energies and the pre-exponential factor from a slope and line intersection of each component were calculated. Results in Table 1 demonstrated the kinetic parameters for all copolymer samples calculated with three various methods.



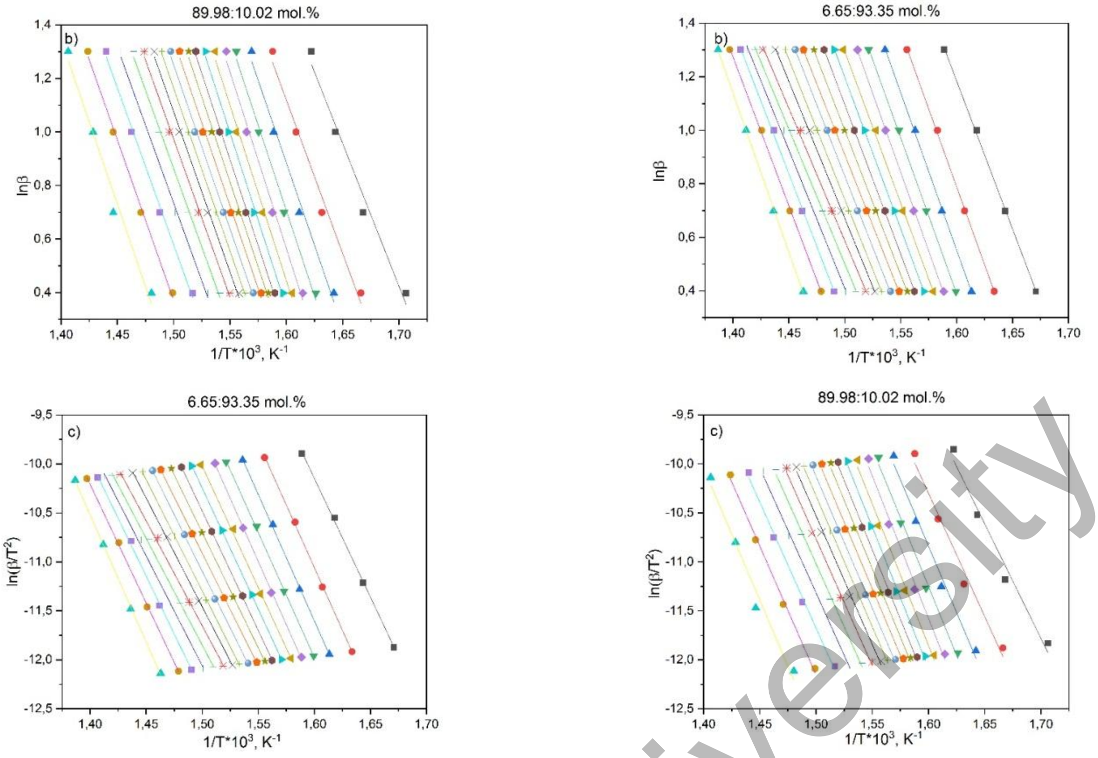


Figure 3. Linearization of thermogravimetry data for copolymers based on p-EGF:MAA at various heating rates, initial ratios (1) of M_1:M_2 in mol. % — 6.65:93.35 mol.%; (2) M_1:M_2 in mol. % — 89.98:10.02 mol. %, in a nitrogen atmosphere, using methods: (a) — Friedman; (b) Flynn-Wall-Ozawa; (c) Kissinger-Akahira-Sunose at various heating rates

Table 1

Dependence of activation energy for thermal decomposition of copolymers based on p-EGF with MAA on transformation degree

α	Ea, kJ·mol^{-1}					
	Flynn-Wall-Ozawa method		Friedman method		Kissinger-Akahira-Sunose method	
	6.65:93.35%	89.98:10.02%	6.65:93.35%	89.98:10.02%	6.65:93.35%	89.98:10.02%
0.05	201.41	194.29	219.41	201.63	201.61	194.33
0.10	211.91	208.89	225.01	237.58	212.42	209.45
0.15	214.03	224.27	215.91	255.77	214.51	225.50
0.20	212.08	232.41	211.32	253.66	212.37	233.96
0.25	214.04	239.91	201.01	241.67	214.35	241.77
0.30	206.29	238.51	196.01	238.54	206.12	240.23
0.35	205.80	237.93	195.45	229.35	205.56	239.55
0.40	203.27	234.20	188.67	219.73	202.83	235.59
0.45	196.73	231.14	180.36	227.65	195.91	232.33
0.50	192.36	225.46	168.19	208.61	191.25	226.29
0.55	193.67	222.93	176.68	200.89	192.56	223.58
0.60	190.63	221.58	175.84	210.04	189.31	222.11
0.65	186.21	218.07	181.55	197.34	184.60	218.39
0.70	180.17	215.04	146.40	199.30	178.16	215.14
0.75	183.10	213.37	207.71	205.50	181.18	213.31
0.80	188.25	212.13	220.50	212.34	186.54	211.93
0.85	197.64	213.83	229.31	217.57	196.36	213.61
0.90	202.70	218.49	228.94	223.36	201.60	218.38
0.95	216.50	224.35	245.71	231.03	215.99	224.41
Average	210.9378	234.8271	211.8925	233.9814	210.185	235.553

Table 1 demonstrates some results of activation energies calculated with using three various methods. The tabular data have a good convergence with less 5% of accuracy. The Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Friedman methods provided to estimate the activation energy in the whole process without a prior assumption of a reaction model.

The choice of these methods permitted to compare the activation energy obtained with the integral and differential methods. Thus, these methods were able to assess the correctness of the accuracy made in deriving of the equations. Figure 3 demonstrates the results of the mathematical processing for the thermogravimetric curves.

In order to define the pre-exponential factor and reaction model, the Achar-Brindley-Sharp methods and method of the invariant kinetic parameters (ABS) were applied [34]. The paper pointed out that the Achar-Brindley-Sharp method were more accurate to calculate the kinetic compensation parameters. Values of *E* and ln*A* were received for all 13 reaction models from Table 1 with using an Equation 4.

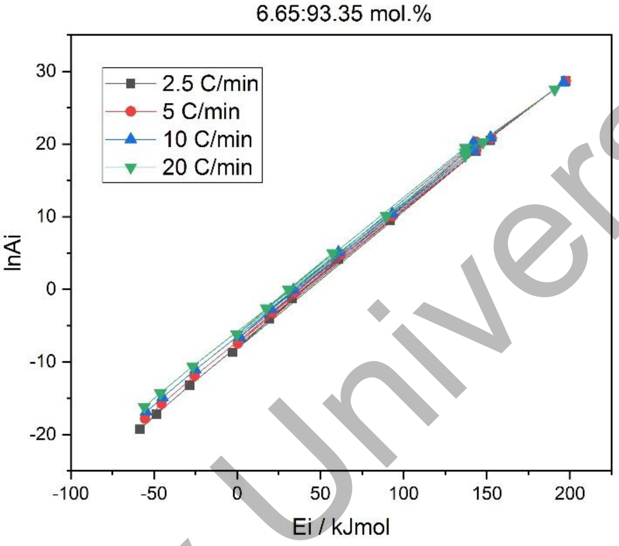


Figure 4. The observed compensation effect between the pre-exponential factor
and apparent activation energy for thermal decomposition of copolymer
based on the p-EGF:MAA, M_1:M_2 in mol.% — 6.65:93.35 mol.%, at various heating rates

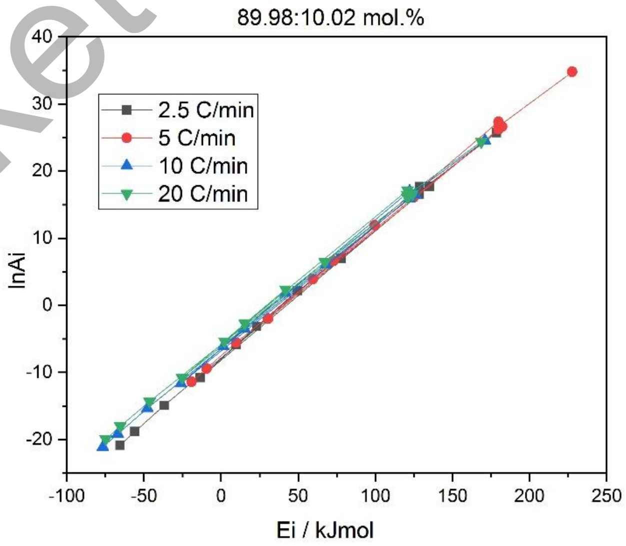


Figure 5. The observed compensation effect between pre-exponential factor
and apparent activation energy for thermal decomposition of copolymer
based on the p-EGF:MAA, M_1:M_2 in mol.% — 89.98:10.02 mol.%, at various heating rates

Figures 4–5 illustrate a correlation between lnA_i and E_i obtained by the compensation effect (CE) with using the Achar-Brindley-Sharp (ABS) method. It was observed that correlation coefficient is close to unity during the using all models (R = 0.99). As a result, it was indicated a good correlation between all parameters regardless of the models used. As expected, the data have a good correlation between all straight lines for all heating rates. Compensation parameters are presented in Tables 2-3.

Table 2

Compensation effect parameters for thermal decomposition of copolymer based on the p-EGF:MAA, M_1:M_2 in mol.% – 6.65:93.35 mol.% at four different heating rates

β (ºC/min)	a^*	b^*	R^2
2.5	0.1887	–7.8780	0.9993
5	0.1853	–7.2247	0.9992
10	0.1822	–6.5555	0.9992
20	0.1787	–5.8623	0.9991

Table 3

Compensation effect parameters of thermal decomposition of copolymer based on p-EGF:MAA, M_1:M_2 in mol.% — 89.98:10.02 mol.% at four different heating rates

β (ºC/min)	a^*	b^*	R^2
2.5	0.1922	–7.8805	0.9993
5	0.1899	–7.4579	0.9993
10	0.1858	–6.5204	0.9992
20	0.1834	–5.8592	0.9992

Figure 6 shows a graph of compensation parameters for copolymers based on p-EGF:MAA, M_1:M_2 in mol.% — 6.65:93.35 mol.% and p-EGF:MAA, M_1:M_2 in mol.% — 89.98:10.02 mol.%.

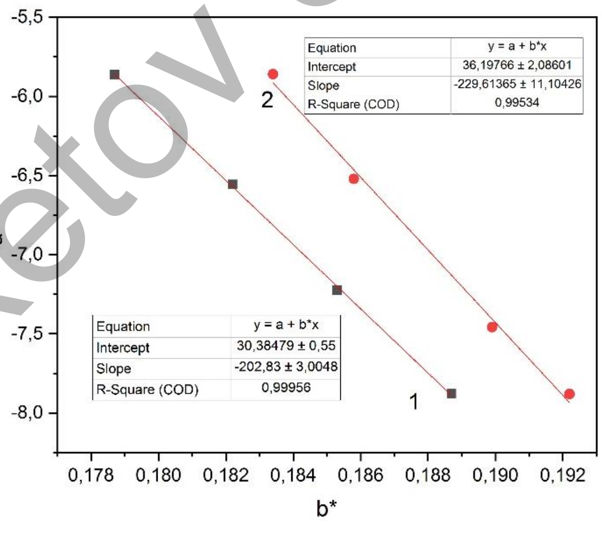


Figure 6. Graph of the correlation ratio of a^* and b^*

The kinetic parameters for copolymer base on p-EGF:MAA were obtained from a slope and line intersection of E and ln$A$. Figure 6 illustrates that activation energy is close to values obtained by the Flynn-Wall-Ozawa, Friedman and Kissinger-Akahira-Sunose methods. They were E = 202 kJ/mol, E = 229 kJ/mol for p-EGF:MAA, M_1:M_2 in mol.% — 6.65:93.35 mol.% and M1:M2 in mol.% — 89.98:10.02 mol.%, respectively.

Using the obtained values of Ei and Ai, the dependence of $g(\alpha)$ on α was plotted in the integral form with using an equation (6) (Fig. 7).

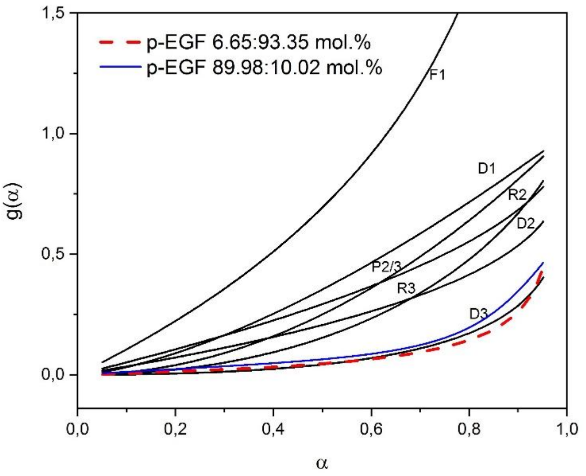


Figure 7. Theoretical curves of $g(\alpha)$ on α for some kinetic models and experimental plot for kinetic model D3 for thermal decomposition of copolymers based on p-EGF:M_1:M_2 in mol.% — 6.65:93.35 mol.% and M1:M2 in mol.% — 89.98:10.02 mol.%, at various heating rates

Figure 7 demonstrates the most appropriate model with a shape as a three-dimensional diffusion (D3).

Thermodynamic parameters

To accurately understand the mechanism of thermal decomposition of the studied copolymers, the changes in entropy (ΔS), Gibbs free energy (ΔG) and enthalpy (ΔH) were calculated. The obtained values were summarized in Tables 4–5.

Table 4

Thermodynamic parameters of thermal decomposition of copolymer based on p-EGF:MAA, M_1:M_2 in mol.% — 6.65:93.35 mol.%

β °C/min	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol*K
2.5	317.38	207.33	–297,26
5	296.78	185.88	–299,53
10	287.00	175.68	–300,69
20	320.87	210.31	–298,63

Table 5

Thermodynamic parameters of thermal decomposition of copolymer based on p-EGF:MAA, M1:M2 in mol.% – 89.98:10.02 mol.%

β °C/min	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol·K
2.5	312.61	204.46	–300.56
5	329.05	221.02	–300.207
10	316.37	207.91	–301.419
20	327.20	218.79	–301.293

The thermodynamic characteristic change of Gibbs energy (ΔG), activation entropy (ΔS) and enthalpy (ΔH) were calculated with using the obtained values of activation energy. A positive value of the Gibbs energy ΔG pointed out infeasibility of the spontaneous decomposition. A negative value of ΔS stated a reduction of random effects at the gas-solid interface and a decrease in the degree of freedom of substances in the thermal decomposition.

Conclusions

The thermal decomposition of a copolymer based on polyethylene glycol fumarate with methacrylic acid was investigated in this paper. Decomposition was observed in different ways with various ratios of the polyester resin in a copolymer composition. Thus, decomposition was much later for copolymer with a large amount of polyester resin. As a result, the activation energy values had higher values.

A good convergence was found in the kinetic parameters of a copolymer obtained by the Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose and Friedman methods. As a result, the received data on activation energy had the similar values at various heating rates.Thus, the process of mass loss intensified with an increase in the heating rate. It was correctly for all non-isothermal processes. The copolymer kinetic triplets were determined and showed good convergence with using methods of the Achar-Brindley-Sharp and invariant kinetic parameters. Graphs of dependence $g(\alpha)$ for various transformation degrees showed a satisfactory fit between the experimental curves and theoretical ones. As a result, the reaction model of two copolymers described with the D3 model was determined.

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