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# Investigation of the destruction of copolymers of poly(ethylene glycol)fumarate with methacrylic acid using differential equations

In the article the thermal characteristics of a copolymer of poly(ethylene glycol)fumarate with methacrylic acid were studied in a dynamic mode in a nitrogen atmosphere for the first time. A kinetic analysis of the thermal destruction process was carried out using three different data processing methods (Freeman-Carroll, Sharp-Wentworth, Achar). Thermodynamic characteristics were also calculated, namely the change in the Gibbs energy (ΔG), enthalpy (ΔH) and entropy of activation (ΔS). The curves of thermogravimetric and differential thermogravimetric analysis of the copolymer were studied in a nitrogen atmosphere at a heating rate of 10 °C/min. The main stage of the copolymer decomposition was found to occur in a narrow temperature range, which is confirmed by a peak in the differential curve. Changes in the reaction rate of the copolymer were shown due to the decrease in the sample mass. It was shown that the results of kinetic analysis depend on the molecular structure of the compounds under study. The activation energies found by the Freeman-Carroll method have lower values, while the Achar and Sharp-Wentworth methods give the same results.

*Keywords:* dynamic thermogravimetry, thermal destruction, copolymer of poly(ethylene glycol)fumarate with methacrylic acid, activation energy.

## *Introduction*

Currently the use of unsaturated polyester resins in industrial countries is promising and profitable, which in turn is due to the relative simplicity of the technology for their production and the low level of financial, material, energy, and labor costs. The presence of unsaturated double bonds in the molecule of unsaturated polyesters allows them to be used as a matrix for obtaining spatially crosslinked copolymers, the formation mechanism of which has been described in many works [1]. This is associated with the necessary stability of weak polyesters to hostile spheres, excellent energy and machine features [2].

Unsaturated polyesters are called hetero- or carbon-chain thermosetting oligomers and polymers containing ester groups and multiple carbon-carbon bonds [3–4]. They are usually obtained from acids and alcohols (or their derivatives) by field condensation or copolymerization of alkylene α-oxides with dicarboxylic acid anhydrides, and at least one reagent must be unsaturated.

Unsaturated polyester resins have a set of useful properties, in particular, they have a lower viscosity, and, they are easier to cure with vinyl monomers in comparison with epoxy resins, which indicates their greater reactivity [5]. The increase in the production of unsaturated polyesters required intensive research into the features of their synthesis, the possibility of copolymerization with other monomers and oligomers, the study of the structure and properties of the obtained copolymers, the search for the most effective methods of their processing and rational areas of application in a weatherometer and a fedeometer. After that, it was found that replacing styrene partially or completely with methyl acrylate improves the color stability of the material and the durability of the first layer to erosion and retains the shine.

Previously, the authors of [6, 7] synthesized polyester resins copolymers, which were used as moisture sorbents and metal-polymer complexes. The acquired knowledge indicates the interdependence of the degradation process on the components' ratio in the copolymer as well as the influence of the environment during the thermal analysis process. It was shown that the results of kinetic analysis depend on the molecular structure of the compounds under study [8].

In this work we investigated the thermal destruction of copolymers of poly(ethylene glycol)fumarate with methacrylic acid in a nitrogen atmosphere.

## *Experimental part*

Poly(ethylene glycol)fumarate was obtained [9] by the polycondensation reaction of maleic anhydride and propylene glycol according to a standard procedure. The progress of the reaction was monitored by determining the acid number.

Copolymers of poly(ethylene glycol)fumarate (p-EGF) with methacrylic acid (MAA) were obtained [9] by copolymerization in a dioxane solution at a monomer mixture.

The study of the thermal properties of the p-EGF:MAA copolymer was carried out on a device for synchronous thermal analysis Labsys Evolution TG-DTA/DSC from Setaram in a dynamic mode in the temperature range of 30–700 °C when heated in an $Al_2O_3$ crucible at a rate of 10 °C/min in an inert nitrogen medium with a flow rate of 30 ml / min. The instrument for thermogravimetric studies and heat flux were calibrated using $CaCO_3$ and in standards, respectively. The experimental data was processed using Microsoft Excel and Processing programs.

A kinetic analysis was carried out in order to determine the kinetic parameters of the decomposition of poly(ethylene glycol)fumarate with methacrylic acid.

*Freeman and Carroll method* [10]. The order of the reaction *n* and the activation energy of the reaction *E* are calculated by the equation:

$$\frac{\left(\frac{E}{R}\right)\Delta\left(\frac{1}{T}\right)}{\Delta\log Wr} = -n + \frac{\Delta\log\left(\frac{dw}{dt}\right)}{\Delta\log Wr}, \tag{1}$$

where $w_r = w_c - w$, $w_c$ is the maximum weight loss; $w$ is the total weight loss by time $t$.

*Sharp and Wentworth method* [11].

$$\frac{\Delta\log\left(\frac{dc}{dt}\right)}{1-c} = \log\frac{A}{\beta} - \frac{E}{RT}, \tag{2}$$

where $c$ is the mass fraction of the sample that reacted during the time $t$; β is a heating rate.

*Achar method* [12].

$$\log\left[\frac{1}{f(\alpha)}\frac{d\alpha}{dt}\right] = \log\frac{A}{\beta} + \frac{E}{RT}, \tag{3}$$

where α is the mass fraction of the sample that reacted during time $t$ and β is a heating rate.

When linearizing the data the calculated points for all samples are placed on straight lines constructed using the least squares method, for which the slope corresponds to $-\frac{E}{R}$, the cut-off section on the ordinate corresponds to the effective order of the reaction.

*Thermodynamic characteristics change in Gibbs energy (ΔG) and activation entropy (ΔS).*

$$\Delta H = E - RT, \tag{4}$$

$$\Delta G = E - RT_{\max}\ln\left(k_B\frac{T_{\max}}{hA}\right), \tag{5}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_{\max}}. \tag{6}$$

Here $k_B$ and $h$ are the Boltzmann and Plank’s constants, respectively. $T_{\max}$ is the temperature, at which the maximum mass loss of the sample occurs.

$$\alpha = \frac{m_i - m_t}{m_i - m_f}, \tag{7}$$

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

## *Results and discussion*

One of the most important applied problems in the chemistry of macromolecular compounds is the creation of heat-resistant polymer and composite materials. Therefore, the most important issue is the possibility of determining the activation energy of thermal decomposition, which is used to characterize the mechanisms of thermal destruction and stability of polymers, including using methods of dynamic thermogravimetry. The main kinetic parameters of the copolymer of poly(ethylene glycol)fumarate with methacrylic acid (p-EGF:MAA) using differential methods (Freeman-Carroll, Sharp-Wentworth, Achar) were determined in the course of the study. Copolymer of poly(ethylene glycol) fumarate with methacrylic acid was heated at 10 °C/min.

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

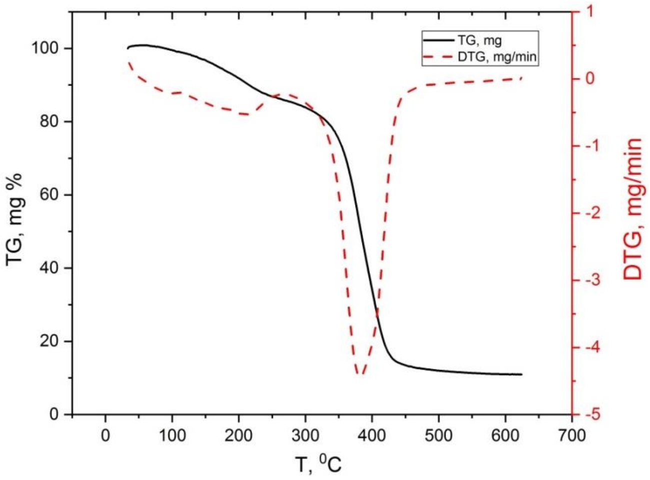
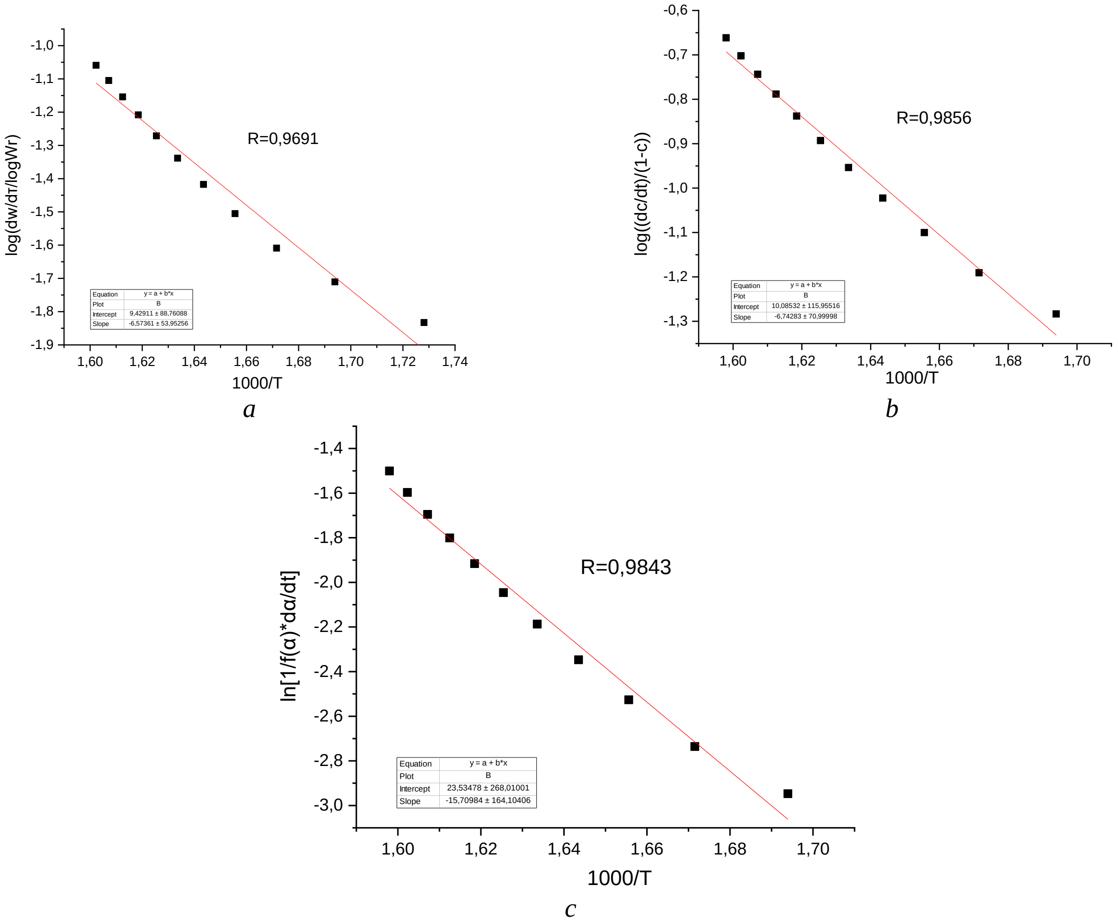


Figure 1. Temperature dependences of weight change (TG curve), rate of weight change (DTG) for p-EGF: MAA copolymer at initial ratios $M_1$:$M_2$, wt% — 6.65:93.35 wt% (under nitrogen atmosphere)



*a*

*b*

*c*

Figure 2. Graphical analysis results determined by the Freeman-Carroll (*a*), Sharp-Wentworth (*b*) and Achar (*c*) methods for the analyzed p-EGF:MAA samples at the M1:M2 ratios, wt.%: 6.65:93.35; with a heating rate of 10 deg/min

In Figure 1 a sample of a copolymer of poly(ethylene glycol) fumarate with methacrylic acid begins to decompose at 200 °C. Then, the beginning of the sample decomposition with the release of volatile substances is observed up to a temperature of about 300 °C. The main stage of the copolymer thermal decomposition occurs from a temperature of ~ 320 °C ~ 430 °C. Then the end of the thermal decomposition process can be observed. In this case, the total weight loss of the sample is ~ 74.42 % of the initial weight. A slight change in the rate of weight loss is observed on the DTG curve in the temperature range of 230–270 °C, followed by a sharp increase with a peak at 375 °C.

Based on the data obtained as a result of thermal analysis of the copolymer, the activation energy values were calculated using the Freeman-Carroll, Sharp-Wentworth and Achar methods. The effective values of the activation energy, preexponents and the order of the destruction reaction were established graphically (Fig. 2).

Comparing the graphs, we can conclude that the points have the greatest scatter for the Freeman-Carroll method (Fig. 2.), which leads to an inaccuracy in the estimation of the activation energy values. The straight line has a slope corresponding to the correlation coefficient R = 0.9691, which is slightly less than the values calculated by the Sharp-Wentworth and Achar methods (Fig. 2).

Table 1 shows the results of the activation energies calculated using three different methods.

Table 1

**Kinetic and thermodynamic parameters of the thermal destruction of the p-EGF-MAA copolymer**

| Methods | $E_a$, kJ/mol | ΔG, kJ/mol | ΔH, kJ/mol | ΔS, kJ/mol | $R^2$ | n |
|---|---|---|---|---|---|---|
| Freeman-Carroll | 122.06 | 71.14 | 119.79 | –178.11 | 0.9691 | 0.32 |
| Sharp-Wentworth | 127.28 | 76.36 | 125.01 | –178.10 | 0.9856 | 0.29 |
| Achar | 128.57 | 77.65 | 126.29 | –178.09 | 0.9843 | 0.28 |

As one can see from the table, the data have excellent convergence with an error of less than 5 %. Using the obtained values of the activation energy, we calculated thermodynamic characteristics change in Gibbs energy (ΔG) and activation entropy (ΔS). We can also observe that the parameters calculated by the Freeman-Carroll method have lower values, while the Achar and Sharp-Wentworth methods give the same results. The positive value of the Gibbs energy ΔG indicates the impossibility of spontaneous implementation of the destruction process.

## *Conclusion*

The kinetic characteristics and thermodynamic parameters of a copolymer of poly(ethylene glycol)fumarate with methacrylic acid have been determined for the first time. Analysis of TG and DTG curves showed sufficient thermal stability of these copolymers in a nitrogen atmosphere. It was found that the main stage of the decomposition of the copolymer occurs in a narrow temperature range, which is confirmed by a peak in the differential curve. The kinetic parameters of the decomposition reaction are calculated by the differential methods, namely Freeman-Carroll, Sharp-Wentworth and Achar methods. The activation energies obtained by these methods have satisfactory convergence. We can also notice that the parameters calculated by the Achar and Sharp-Wentworth methods give more accurate results. In this regard, we recommend application of exactly two of these methods.

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## Полиэтиленгликольфумараттың метакрил қышқылымен сополимерлерінің деструкциясын дифференциалдық теңдеулер қолдану арқылы зерттеу

Мақалада полиэтиленгликольфумараттың метакрил қышқылымен сополимерінің динамикалық режимдегі, азот атмосферасындағы термиялық сипаттамалары алғаш рет зерттелінген. Мәліметтерді өңдеудің үш әртүрлі әдістерін (Фримен-Кэррол, Шарп-Уэнтворт, Ахар) қолдана отырып, термиялық деструкция процесіне кинетикалық сараптау жүргізілді. Сонымен қатар, термодинамикалық сипаттамалар — Гиббс энергиясының өзгеруі (ΔG) энтальпия (ΔH) және активация энтропиясы (ΔS) есептелінді. Сополимердің термогравиметриялық және дифференциалдық термогравиметриялық сараптама қисықтары азот атмосферасында қыздыру жылдамдығы 10°С/мин кезінде зерттелінді. Сополимердің температураның тар интервалында жүрген және дифференциалдық қисықтағы шыңмен дәлелденген ыдырауының негізгі кезеңі анықталды. Үлгінің массасының азаюымен байланысты сополимердің реакция жылдамдығының өзгеруі көрсетілді. Кинетикалық сараптау нәтижелерінің зерттелінген қосылыстардың молекулалық құрылымына байланыстылығы көрсетілген. Фримен-Кэррол әдісімен табылған активация энергиясының мәні төменірек шамаға ие, ал Ахар мен Шарп-Уэнтворт әдістері бірдей нәтижелер береді.

*Кілт сөздер*: динамикалық термогравиметрия, термиялық деструкция, полиэтиленгликольфумараттың метакрил қышқылымен сополимері, активация энергиясы.

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## Исследования деструкции сополимеров полиэтиленгликольфумарата с метакриловой кислотой с использованием дифференциальных уравнений

В статье впервые изучены термические характеристики сополимера полиэтиленгликольфумарата с метакриловой кислотой в динамическом режиме, в атмосфере азота. Проведен кинетический анализ процесса термической деструкции с использованием трех разных методов обработки данных (Фримена–Кэрролла, Шарпа–Уэнтворта, Ахара). Также были рассчитаны термодинамические характеристики — изменение энергии Гиббса (ΔG), энтальпии (ΔH) и энтропии активации (ΔS). Кривые термогравиметрического и дифференциального термогравиметрического анализа сополимера были изучены в атмосфере азота при скорости нагревания 10ºС/мин. Были установлены основные этапы разложения сополимера, происходящие в узком интервале температур, который подтверждается пиком на дифференциальной кривой. Были показаны изменения скорости реакции сополимера в связи с убыванием массы образца. Показано, что результаты кинетического анализа зависят от молекулярной структуры исследуемых соединений. Значения энергии активации, найденные методом Фримена–Кэррола, имеют более низкие значения, а методы Ахара и Шарпа–Уэнтворта дают одинаковые результаты.

*Ключевые* слова: динамическая термогравиметрия, термическая деструкция, сополимер полиэтиленгликольфумарата с метакриловой кислотой, энергия активации.

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