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*Article*

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# Study of thermal stability and determination of effective activation energy values during degradation of unsaturated polyester copolymers in the air atmosphere

The study of the kinetic parameters of copolymers based on polyethylene glycol fumarates, as well as the external and internal effects on them, is essential for production processes at various levels. This will solve a whole range of issues in the field of the shelf life of materials and storage conditions. All these point to the relevance of this research. The authors of the research attempt to test the most common thermogravimetric data processing methods and to improve them in terms of the quality of the predictive capabilities of the resulting regression equation. Both of them are important for the production of initial components and the manufacture of the final product from the studied materials. Therefore, the study and further use of the numerical data of the TG/DTA curves applies to both theoretical and practical branches of science. Thus, summarizing the experimental data on the thermal stability studies, we assume that p-EGF: AA copolymers with compositions of 21.03:78.97 and 68.96:31.04 wt.% have a relatively high degree of resistance to heating. It was found that the calculation by the FR method agreed well with the results of the KAS method. It should be noted that for the p-EGF: AA copolymer (21.03:78.97 wt.%) at heating rates of 5.0, 10.0, 20.0 °C·min$^{-1}$, the average activation energy data obtained for two methods increase in the following series: $\bar{E}_{KAS}$ = 187.34 kJ /mol < $\bar{E}_{FR}$ = 200.17 kJ/mol.

*Keywords:* thermogravimetry, thermal analysis, kinetic parameters, copolymers, polyethylene glycol fumarate, acrylic acid, activation energy, polyesters.

## *Introduction*

Previously, we have developed methods for producing unsaturated polyester resins [1]. By implementing radical co-and terpolymerization of ionic monomers, a number of cross-linked polymers with a mesh structure were obtained, which can be used as hydrogels in vegetable crops. Also, the main kinetic parameters of the decomposition of some of the above copolymers were identified using differential and integral methods [2, 3]. The research result showed the practical value of this technique. It should be noted that, before our study, the process of studying the thermal stability of unsaturated polymers had not yet been considered by experts.

An integral part of the research is that no domestic or international professional literature has yet been developed that allows the most accurate prediction of the composition of polymeric materials and their kinetic properties. Determining the properties of kinetic polymers is a complex process in which many external factors have to be considered, especially thermal exposure, which requires significant time, material and physical cost. With the help of data, the prediction accuracy will increase, and the process itself will become less costly and time-consuming.

The main purpose of this work is to conduct a thermal analysis [4] of unsaturated polyester resin copolymers of various compositions in the atmosphere and to interpret the kinetic parameters obtained as a result of mathematical processing of thermogravimetric data.

## *Experimental*

The study of the thermal decomposition of the copolymer of polyethylene glycol fumarates with acrylic acid was carried out on a differential scanning calorimeter LABSYS$^{TM}$ EVO 1600 °C SETARAM, (France) in dynamic mode in the temperature range of 30–1000 °C at heating rates 5.0, 10.0, 20.0 °C·min$^{-1}$ in the purified air environment, at a speed flow 30 mL/min. The device calibration for thermogravimetric studies and heat flux was performed according to $CaCO_3$ and In (Indium) standards, respectively.

As a rule, the differential kinetic equation for the thermal decomposition process can be written as follows:

$$\ln\left(\beta\frac{d\alpha}{dT}\right)_{\alpha}=\ln\left[Af(\alpha)\right]-\frac{E}{RT} \qquad (1)$$

The expression on the right side of the equation contains an exponential function and this expression cannot be represented as an analytical function. The solution can be the search for some approximation [5]. In practice, the most common way to overcome this difficulty is to use the following methods:

a) The Friedman method (FR) [6] is considered a "model-free" method, since f(α) is not explicitly specified.

b) The main equation of the Kissinger-Akahira-Sunose (KAS) method [7, 8] is as follows: $\ln\left(\beta/T^{2}\right)=\ln\left[AE/\left(Rg(\alpha)\right)\right]-E/RT$

The choice of methods is due to the possibility of comparing the activation energy obtained by differential and integral methods, which makes it possible to assess the validity of the assumptions made when deriving these equations. The results of the FR and KAS methods are systematized in Table 1 the graphical interpretation is shown in Figure 3.

*Results and Discussion*

In this work, the objects of study were previously synthesized copolymers of polyethylene glycol fumarate with acrylic acid with compositions of 21.03:78.97 and 68.96:31.04 wt.%. Figure 1 demonstrates the results of thermogravimetric analysis of these copolymers.

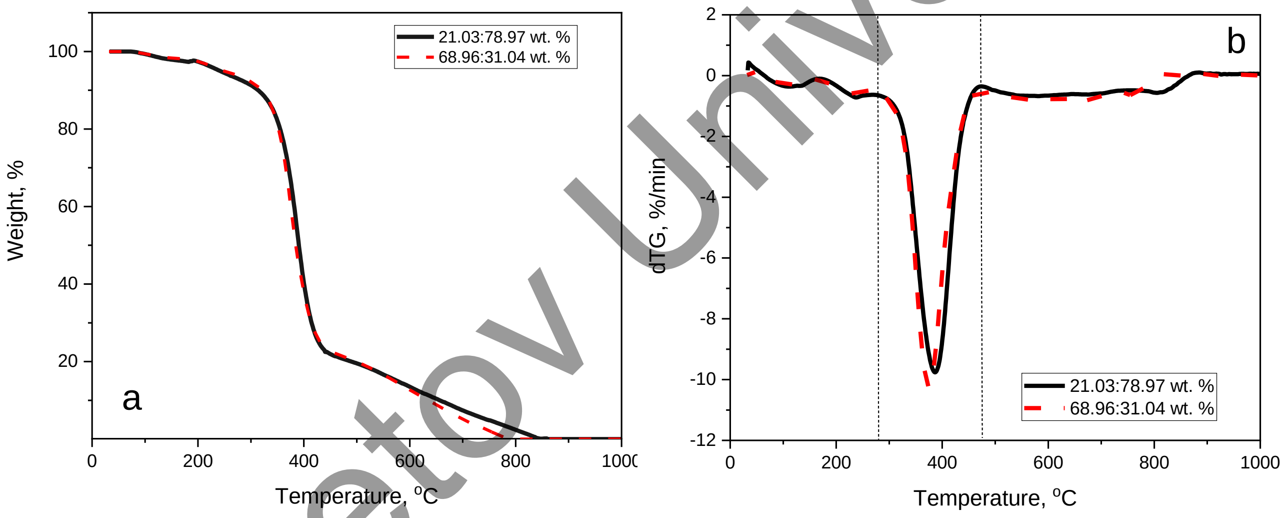

Figure 1. Dependences of samples mass on temperature (*a*) and mass change rate (*b*) of p-EGF:AA copolymers at a heating rate of 10 °C/min

Figure 1 indicates the thermograms of copolymers of p-EGF:AA composition 21.03:78.97 and 68.96:31.04 wt.%. It is shown that the copolymers of p-EGF:AA (21.03:78.97 and 68.96:31.04 of the wt.%) are resistant to 1000.0 °C, while the copolymers are observed exothermic effect $T_{initial}$ = 277 ± 0.1 °C (at 386 °C) for p-EGF:AK (21.03:78.97) and $T_{initial}$ = 265.0 ± 0.1 °C (at 375.0 °C). The low-temperature peak is associated with the cleavage of crystallization water, the second peak is explained by the destruction of the main chains, which proceeds by random rupture model. The p-EGF:AK copolymers composites 21.03:78.97 and 68.96:31.04 wt.% (Figure 1, *b*) are resistant at 1000.0 °C, from 10 % to 15 % weight loss at 200.0 °C. The residual weight is 58–60 %.

Table 1

**Thermogravimetric data for copolymers 21.03:78.97 and 68.96:31.04 wt.%**

| Copolymer | $T_{initial}$(°C) | $T_{peak}$(°C) | $T_{final}$(°C) |
|---|---|---|---|
| 21.03:78.97 wt.% | 277 | 386 | 472 |
| 68.96:31.04 wt.% | 265 | 375 | 470 |

To determine the activation energy of the thermal decomposition process, the main stage of the copolymer decomposition was chosen (Figure 1b). Figure 2 (*a*, *b)* shows the decomposition degree.

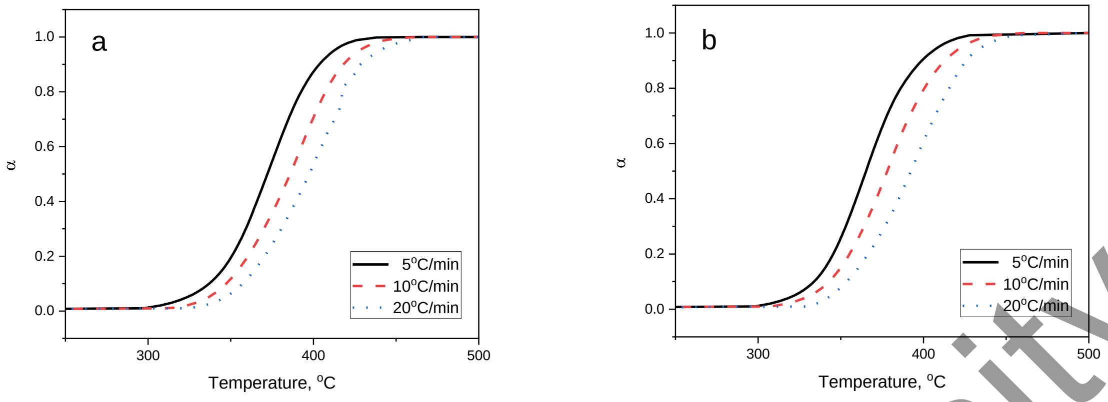

Figure 2. Dependence of conversion degree α on temperature of p-EGF:AA copolymers 21.03:78.97 (*a*) and 68.96:31.04 (*b*) at different heating rates

As can be seen from Figure 2, the calculated values of the degree [9] of transformation have a similar conversion nature. However, there is a delay in the decomposition process with an increasing heating rate. This can be seen from the shift in the initial temperature from 300 °C to 330 °C for lower and higher heating rates, respectively. Kinetic parameters obtained from the slope and intersection of the straight lines are presented in Table 1; graphical interpretation is shown in Figure 3.

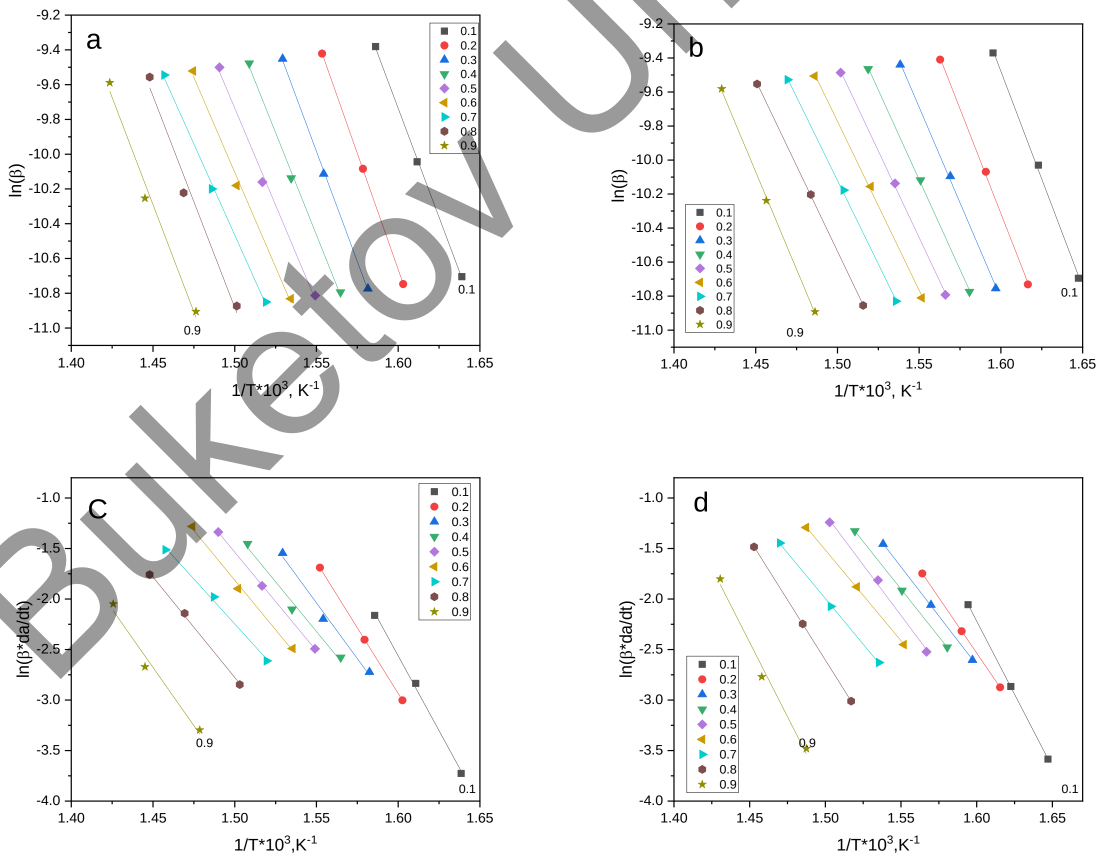

Figure 3. Graphical dependences of Kissinger-Akahira-Sunose (*a*, *b*) and Friedman (*c*, *d*) equations for the p-EGF:AK copolymer at 21.03:78.97 and 68.96:31.04 wt.% ratios

The curves (Figure 3) obtained by the KAS and FR methods for p-EGF:AA copolymers at 21.03:78.97 and 68.96:31.04 wt.% ratios are linear, which means that both methods provide reliable results regarding their thermal decomposition kinetics. The conclusion further [10] is supported by the fact that the activation energies calculated by both methods agree relatively closely (Table 1). This experimental result suggests that both the composition and, most importantly, the ability of NPS (polyethylene glycol fumarate) to form copolymers with acrylic acid (AA) play an important role in determining the thermal degradation kinetics of p-EGF: AA copolymers. The fact that in the FR method [6] (model-free analysis) f(α) is a constant value, while the logarithm of the conversion rate $\ln\left[\beta\left(d\alpha/dT\right)\right]$ is considered as a function of the corresponding temperature at any fixed value of α. In contrast, in the KAS method [7, 8] (integral method), the determination of kinetic triplets is based on determining the temperature (T) corresponding to a certain, derivatively chosen value of the degree of conversion (α) at various heating rates (β). Analysis of the obtained results (Figure 4) led to the conclusion that the FR and KAS methods make it possible to determine the kinetic characteristics of the decomposition of p-EGF:AA copolymers.

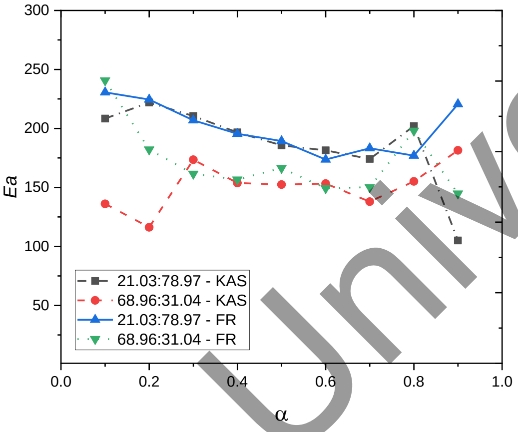

Figure 4. Activation energies according to Kissinger-Akahira-Sunose (KAS) and Friedman (FR)

Comparing the data (Figure 2) from the KAS and FR approaches, it can be noted that the results for activation energies are similar. Nevertheless, the first method (KAS) provides activation energies ($\overline{E}$) values which are10 % lower than those of the FR method. This makes sense because these methods are based on relatively different approximations. However, the FR equation provides more reliable and accurate results than the KAS equation [11].

### *Conclusions*

The thermostability and thermal decomposition kinetics of copolymers of polyethylene glycol fumarate with acrylic acid (21.03:78.97 and 68.96:31.04 wt.%) were first studied by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). A new direction of application in the identification of copolymers, as well as in the development of production technology [12] and safe disposal of macromolecular substances based on NPS (polyethylene glycol fumarate), was investigated. These parameters were determined based on FR and KAS methods, which have good convergence. It was shown that thermostability decreases in the following order: p-EGF:AA (21.03:78.97) > p-EGF:AA (68.96:31.04). Based on the study of TG/DTG curves for copolymers of polyethylene glycol fumarate with acrylic acid of two different compositions 21.03:78.97 and 68.96:31.04 wt.%, it can be assumed that these compounds have a relatively high degree of heat resistance. Under the influence of oxygen, the copolymers are completely decomposed to high temperatures without a carbon residue. It was also found that the copolymer with a high content of polyester resins exhibits less activity.

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# Ауа атмосферасындағы қанықпаған полиэфир сополимерлерінің деградациясы кезінде жылу тұрақтылығын зерттеу және активтендіру энергиясының тиімді мәндерін анықтау

Полиэтиленгликольфумарат негізіндегі сополимерлердің кинетикалық көрсеткіштері, сондай-ақ, оларға ішкі және сыртқы әсер ету саласындағы зерттеулер әр түрлі деңгейдегі өндірістік процестер үшін өте маңызды. Бұл материалдардың жарамдылық мерзімі мен оларды сақтау шарттары саласындағы бірқатар мәселелерді шешеді. Мұның бәрі осы зерттеудің өзектілігін көрсетеді. Жұмыста термогравиметриялық деректерді өңдеудің және олардан алынған регрессиялық теңдеудің болжамды мүмкіндіктерін сапасы тұрғысынан жетілдірудің кең таралған әдістерін тексеруге әрекет жасалған. Сонымен қатар, бұл көрсеткіштер бастапқы компоненттерді өндіру үшін де, зерттелетін материалдардан түпкілікті өнімді жасау үшін де өте пайдалы. Сондықтан ТГ/ДТА қисықтарының сандық деректерін зерттеу және одан әрі қарай пайдалану ғылымның теориялық және практикалық салалары үшін маңызы бар. Осылайша, термиялық тұрақтылығын зерттеу бойынша эксперименттік деректерді жинақтай отырып, құрамы 21.03:78.97 және 68.96:31.04 болатын п-ЭГФ:АК сополимерлерінің қыздыруға төзімділігін салыстырмалы түрде жоғары дәрежеге ие деп болжанады. Сондай-ақ, ФР әдісі бойынша есептеулер, КАС әдісінің есептеу нәтижелерімен жақсы сәйкесетіндігі анықталды. п-ЭГФ: АК сополимері үшін (21.03:78.97 масс. %) 5.0, 10.0, 20.00 С. мин$^{-1}$. қыздыру жылдамдығы кезінде активтендіру энергиясы бойынша алынған орташа деректер екі әдіс үшінде мына қатарда артады: $\bar{E}_{\text{КАС}} = 187.34$ кДж/моль $<\bar{E}_{\text{ФР}} = 200.17$ кДж/моль.

*Кілт сөздер:* термогравиметрия, термиялық анализ, кинетикалық параметрлер, сополимерлер, полиэтиленгликольфумарат, акрил қышқылы, активтендіру энергиясы, полиэфирлер.

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# Изучение термической стабильности и определение эффективных значений энергии активации при деградации сополимеров ненасыщенных полиэфиров в атмосфере воздуха

Исследования в области кинетических показателей сополимеров на основе полиэтиленгликольфумаратов, а также внешнего и внутреннего воздействия на них очень важны для производственных процессов самого различного уровня. Это позволит решить целый спектр вопросов в области срока годности материалов и условий их хранения. Все это указывает на актуальность данного исследования. В статье предпринята попытка проверки наиболее распространенных методов обработки термогравиметрических данных и их совершенствования с точки зрения качества прогнозирующих возможностей получаемого регрессионного уравнения. В то же время данные показатели очень важны как для производства исходных компонентов, так и для изготовления конечного продукта из исследуемых материалов. Поэтому исследование и дальнейшее использование числовых данных кривых ТГ/ДТА имеет актуальное значение как для теоретической, так и для практической отраслей науки. Таким образом, обобщая экспериментальные данные по изучению термической стабильности, авторы приходят к выводу, что сополимеры п-ЭГФ: АК составом 21.03:78.97 и 68.96:31.04 масс, % обладают относительно высокой степенью устойчивости к нагреванию. Кроме того, было установлено, что, рассчитанные по методу ФР хорошо согласуются с результатами расчета с применением метода КАС. Следует отметить, что для сополимера п-ЭГФ:АК (21.03:78.97 масс, %) при скоростях нагрева 5.0, 10.0, 20.0 °С·мин$^{-1}$полученные средние данные по энергии активации увеличиваются для двух методов в следующем ряду: $\bar{E}_{КАС}$=187.34 кДж/моль <$\bar{E}_{ФР}$= 200.17 кДж/моль.

*Ключевые слова*: термогравиметрия, термический анализ, кинетические параметры, сополимеры, полиэтиленгликольфумарат, акриловая кислота, энергия активации, полиэфиры.

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