ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD) in the educational program "8D05301 – Chemistry"

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Study of the process of thermal degradation of the copolymers based on polyethylene glycol fumarate with acrylic acid

General characteristics of the work. The dissertation is devoted to studying the characteristics of thermochemical transformations during the thermal degradation of polyethylene glycol fumarate copolymers with acrylic acid. The work carried out an experimental study of the kinetics and mechanism of decomposition of copolymers.

The relevance of the dissertation work. Currently, there is a constant demand for new materials with unique and valuable properties. An exhaustive study of the process of thermal degradation of polymers can lead to the development of new materials with improved characteristics. Understanding the mechanisms of thermal degradation will help optimize the processes of recycling and recycling of polymer materials. The data obtained during the research can be useful for various industries, medicine, agriculture, etc.

Purposeful creation of new polymeric substances (polyesters) and prediction of their properties is impossible without reliable methods for predicting the thermokinetic characteristics of these substances. Forecasts are reliable only when accurate kinetic analysis methods are used. Of particular interest are the parameters of the Arrhenius equation (the pre-exponential factor and the activation energy). The value of activation energy for thermal decomposition is one of the most important indicators that characterize the resistance of polymers to high temperatures. It is used in the study of the mechanisms of thermal decomposition, aging and stabilization of polymer materials. This leads us to a class of works aimed at establishing mathematical relationships between the speed of the process, degree of conversion, and temperature using data from thermogravimetric analysis (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC).

The simplest way is to define a kinetic triplet, a term often used to describe a single set of A, E_a and $f(\alpha)$ or $g(\alpha)$. Reactions involving solids, including thermal decomposition reactions, belong to a special class of topochemical processes characterized by localization of the reaction zone of the solid reagent and the reaction product.

For many years, the Department of Organic Chemistry and Polymers at Karaganda Buketov University has successfully conducted research on the synthesis and investigation of the properties of unsaturated polyester resin copolymers. This is reflected in numerous publications in highly rated journals. Previously, we synthesized copolymers by radical copolymerization of unsaturated polyester resins

with a number of unsaturated carboxylic acids. These copolymers have carboxyl groups in their side chains and are sensitive to various environmental changes.

This dissertation work is a continuation of research work aimed at studying the physicochemical properties of copolymers based on polyethylene glycol fumarate and acrylic acid with different ratios of initial monomers.

The purpose of the dissertation is to study the processes occurring during the thermal decomposition of copolymers based on polyethylene glycol fumarate with acrylic acid. It also aims to study how various factors affect the kinetics of these thermal degradation processes, and create mathematical models to account for them.

Research objectives:

-to study the composition and physico-chemical properties of synthesized copolymers of polyethylene glycol fumarate with acrylic acid;

-to predict the behavior of copolymers in various liquid media using kinetic methods and differential scanning calorimetry;

-to identify the mechanism of formation of the polymer matrix structure using a scanning electron microscope;

-to determine the elemental composition of copolymers of polyethylene glycol fumarate with acrylic acid of various compositions and degradation products;

-to determine the kinetic parameters of thermal decomposition using the linear differential methods of Freeman-Carroll, Achar, Sharp-Wentworth and the Coates-Redfern integral method;

-to determine the kinetic and thermodynamic parameters of the process of thermal decomposition of copolymers, using linearization of kinetic data, iso-conversion methods and means of nonlinear approximation, is necessary;

-to study the mechanism of thermal decomposition of p-EGF copolymers by physico-chemical analysis of the degradation products;

-to determine the kinetic and thermodynamic parameters of the process of thermal decomposition of copolymers using regression analysis.

-to develop software to automatically construct a mathematical model of the thermal destruction process.

Objects of research. The copolymers of polyethylene glycol fumarate, synthesized by us using acrylic acid in equimolar ratios of three, were used as the objects of this research. (7,95:92,05 mol. %, 44,05:55,95 mol.%, 89,05:10,95 mol.%).

Research methods - thermogravimetric analysis, differential scanning calorimetry, gel permeation chromatography, nuclear magnetic resonance, scanning electron microscopy, infrared spectrometry, chromatographic mass spectrometry, differential kinetic methods, Coates-Redfern integration method, Friedman, Flynn-Ozawa, Wall isoconversion method, non-parametric kinetics, regression analysis, statistical processing of results.

Substantiation of the novelty and significance of the results obtained:

- the kinetic characteristics and thermodynamic parameters of polyethylene glycol fumarate copolymers with acrylic acid have been determined for the first time using non-isothermal thermogravimetry data. The use of various methods, such as integral, differential, isoconversion and regression, allowed us to obtain more

accurate and complete data on the kinetics and thermodynamics of polymer decomposition. This, in turn, plays a key role in understanding the stability and durability of materials, which is important for their practical application;

- For the first time, the mechanism of decomposition of polyethylene glycol fumarate copolymers with acrylic acid was studied using various physicochemical analysis methods. The mechanism of polymer decomposition provides information on the ways and products of degradation, which opens up opportunities for creating environmentally friendly and functional materials in various industries. This can also be especially important for developing new biodegradable materials and optimizing their properties;

- The results of this study can be used to develop an algorithm for creating mathematical models of polymer thermal degradation. Based on these results, software was created that automates the process of calculating kinetic parameters. This software simplifies and speeds up the processing of thermogravimetric data, improves the accuracy and reproducibility of research, and is useful for both basic research and applied tasks in the fields of polymer and composite materials;

Compliance with the directions of scientific development or government programs. The work was carried out within the framework of program-targeted financing on the topic: "Development of new sealants and adhesives based on unsaturated polyester resins for the needs of construction and defense industries (2021-2023, BR10965249-OT-23)."

Theoretical and practical significance. This research provides an opportunity to significantly optimize existing methods of thermal analysis both within our republic and globally. Positive results of practical research can solve many problems both in methodology and in practical production of polymer resins. The study of thermal analysis is becoming an increasingly important factor in the study of high-molecular-weight materials. In this regard, it is necessary to develop recommendations for collecting thermal analysis data for kinetic calculations, which contribute to the improvement and more accurate operation of thermal analyzers. This will optimize the parameters for registering thermograms and their subsequent processing. Today, specialists involved in the production of thermal equipment typically use highly specialized techniques and software, which does not always solve all problems in general.

The main provisions submitted for protection are:

1. The influence of various factors (temperature, presence of solvents, salts, exposure time) on swelling and thermal stability of copolymers of polyethylene glycol fumarate with acrylic acid has been studied.

The maximum degree of swelling is a max = 305,81% for the copolymer p-EGF:AA 7,95:92,05 mol. %. With swelling of the polymer p-EGF:AA 89,05:10,95 mol. % in salt and fresh water, invariant kinetic parameters have low values and increase with decrease in proportion of unsaturated polyester resin in composition of copolymer. The results of differential scanning calorimetry show that swollen copolymers of p-EGF:AA composition 7,95:92,05 mol. % release water during thermal decomposition with heat absorption during (1259,917 J/g in pure and 795,441 J/g in dirty water).

2. The kinetics of thermal decomposition of polyethylene glycol fumarate copolymers with acrylic acid were studied using differential methods, including Achar, Sharp-Wentworth, and Freeman-Carroll, based on non-isothermal data. The activation energy values calculated by these methods in an inert medium for the p-EGF:AA 7,95:92,05 mol.% copolymer range from 104~153 kJ/mol, and for the p-EGF:AA 89,05:10,95 mol.% ratio, the values are within 90~130 kJ/mol (15-20% lower in the air atmosphere)

3. The kinetics of thermal decomposition of polyethylene glycol fumarate copolymers with acrylic acid were studied using differential methods, including Achar, Sharp-Wentworth, and Freeman-Carroll, based on non-isothermal data. Thermal analysis of p-EGF:AK copolymer with ratios 7,95:92,05 and 89,05:10,95 mol. % showed that thermal degradation of the copolymers occurred in the range of 150-550°C (in nitrogen) and 15-700°C (in air). The activation energies obtained from different models varied slightly and practically did not depend on the experimental conditions under which thermal destruction took place.

4. The thermodynamic and kinetic parameters of the thermal decomposition of copolymers of polyethylene glycol fumarate with acrylic acid were determined using non-linear approximation. The kinetic parameters obtained by different methods showed good convergence. The activation energy values for the thermal decomposition process of the p-EGF copolymer with a composition of 7,95:92,05 mol. % (Ea=204,10 ± 1,16 kJ/mol) were higher than those of the copolymer p-EGA with a composition 89,05:10,95 mol. % (Ea =199,21 ±11,06 kJ/mol). The mechanism of thermal decomposition of the copolymers has been investigated. Destruction of compounds begins with the removal of water molecules from the cavity, then acrylic acid, after which thermal degradation of unsaturated polyester resin occurs. Destruction copolymers at high temperatures mainly proceeds through the ether bonds of polyethylene glycol fumarate with a significant amount of CO_2 released.

The author's personal contribution includes conducting experimental work (synthesis, sample preparation, analysis using physico–chemical methods), searching for and generalizing literary data, processing research results, and discussing the results with the scientific adviser and foreign consultants. The doctoral student's contribution to the preparation of each publication includes conducting a literary and patent search, interpreting the results obtained, corresponding with the editorial boards of journals and reviewers, and writing articles.

1. «The use of differential calculation methods for the destruction of copolymers of polyethylene glycol fumarate with the acrylic acid» https://doi.org/10.31489/2020Ch3/4-10- thermogravimetric analysis of copolymers in various media, calculation of the activation energy of thermal decomposition using differential Freeman-Carroll, Achar, and Sharp-Wentworth methods.

2. «Integral Ways of Calculating the Destruction of Copolymers of Polyethylene Glycol Fumarate with Acrylic Acid»https://doi.org/10.1134/S0036024421100034- thermal analysis of copolymers, calculation of the activation energy using the integral Coates-Redfern and Kissinger-Akahira-Sanz methods.

3. «Study of Thermal Decomposition of the Copolymer Based on Polyethylene Glycol Fumarate with Acrylic Acid» https://doi.org/10.1155/2022/3514358 - synthesis of copolymers, thermogravimetric analysis, calculation of activation energy of thermal destruction by the Friedman and Kissinger-Akahira-Sanuz methods; determination of kinetic parameters using invariant kinetic parameters.

4. «Kinetic parameters of thermal destruction of the copolymer of polyethylene glycol fumarate with acrylic acid in inert medium»https://doi.org/10.15328/cb1260 - thermal analysis of copolymers in an inert medium, calculation of the activation energy of thermal decomposition using the Friedman and Kissinger-Akahira-Sanuz methods, determination of the pre-exponential multiplier and reaction model using the method of invariant kinetic parameters.

5. «Study of thermal stability and determination of effective activation energy values during degradation of unsaturated polyester copolymers in the air atmosphere»https://doi.org/10.31489/2022Ch1/86-91- thermogravimetric analysis of copolymers in an air environment and calculation of the activation energy for thermal decomposition using isoconversion techniques.

6. «Effect of Heat Treatment on the Supramolecular Structure of Copolymers Based on Poly (propylene glycol fumarate phthalate) with Acrylic Acid»https://doi.org/10.31489/2959-0663/2-24-9 - synthesis of copolymers, thermogravimetric analysis of copolymer, preparation of pyrolysis products from samples, description of the mechanism of thermal decomposition based on physicochemical analysis methods for the copolymer.

Publications and approval of the work. 6 papers were published on the topic of the dissertation, including 4 articles in journals recommended by the Quality Assurance Committee of Science and Higher Education at the Ministry of Education and Science of the Republic of Kazakhstan (Karaganda University Bulletin, Chemical Bulletin Kazakh National University) and 2 articles published in international peer-reviewed journals indexed in Web of Science and Scopus databases (Russian Journal of Physics Chemistry A, Q4; Journal of Chemistry, Q3).

The results of the work were presented at international conferences: "Investigation of thermal decomposition of copolymers of polyethylene glycol fumarate with acrylic acid", Modern problems of polymer science: Uzbekistan-Kazakhstan Symposium (Tashkent, 2020), "Gel-penetrating chromatography in the study of unsaturated polyester resins" and "Theoretical and experimental chemistry": Materials of the VII International Scientific and Practical Conference (Karaganda, 2013). According to the results of the study, the computer software "Thermo Grav Activation Energy" was developed and a certificate for entering information into the state register of copyrights (No. 40925) was issued.

The structure and scope of the dissertation. The dissertation is presented on 141 pages and includes 17 tables, 52 figures, and a list of 213 sources (domestic and foreign). The work consists of an introduction, main part (including a literature review, practical work, results, and discussion), conclusion, and appendix.