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Cure kinetics of pultruded vinyl-ester resins

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Cure kinetics of pultruded vinyl-ester resins

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ABSTRACT

Pultrusion is a high production process allowing the fabrication of high-performance composite profiles of the constant cross-section. As the process is automated and virtually independent of human factor influence, the quality of the product will be determined by the correct selection of processing parameters at the start of the manufacturing process. In order to find optimum processing parameters, e.g., pulling speed, die block temperature, etc., the simulation of the resin curing process is used. Typically, engineers use the same models applied in the simulation of other composite manufacturing processes, such as vacuum infusion, molding, etc. However, these mathematical models are not ideally suited for the pultrusion process due to the influence of friction-reducing additives on the process kinetics.

The development of the pultrusion industry all over the world and the desire to increase production rates stimulate the search for new approaches to simulation and optimization of pultrusion production. The presented work aims to describe the effect of technological additives, modelling the kinetics of resin polymerization considering technological additives, and studying the effect of additives on the simulation of pultrusion composite profile production.

In the course of the work, data obtained from a differential scanning calorimeter describing the polymerization kinetics of Atlac 430 resin with different technological additives was analysed. Measuring of DSC was carried out in accordance with ISO 11357-1209. The polymerization kinetics was described for the obtained mixtures, and the pultrusion process was simulated.

ACKNOLEGEMENTS

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Introduction

Pultrusion is a highly efficient manufacturing process that allows the production of high-performance composite profiles of constant cross-section. Such products have many advantages: they are light and durable, like other composites. Moreover, automatization allowed mass production of the composite profile up to 5 m/min[1], which reduced its cost. The field of application of pultrusion composites is wide - some of the significant composite markets include automobiles, rail transport, aerospace, and wind turbine blades. Composite profiles have the potential to replace some of the classic materials used in the construction industry, due to many advantages over traditional materials, such as a high strength-to-weight ratio, high corrosion resistance, and excellent electrical and thermal insulation properties. These unique properties have made pultrusion composites widely used in bridge construction for the manufacture of profiles or decking.

The main problem of pultrusion production is to find a balance between quality and productivity. The fiber pulling speed limits the daily amount of composite produced. At the same time, the pulling speed is limited by the composite curing rate. On the one hand, with a significant increase in the pulling speed, the composite produced does not have time to harden completely. This will lead to deformation and reduction in the quality of the products. On the other hand, too much deceleration of the pulling speed reduces the overall speed of product production, which is unprofitable from an economic point of view. Simulation of composite curing will allow you to configure the pultrusion process so that the speed of composite production is necessary and enough. This approach will allow to produce high-quality composite material with maximum extraction speed.

Simulating composite curing under the influence of temperature is based on models of resin polymerization. This paper describes the simulation of pultrusion resin polymerization considering the production features in order to optimize the pultrusion production of composite products

The purpose of this work is to refine the resin polymerization model for subsequent simulation of pultrusion production. The tasks are to study the effect of technological additives on the kinetics of pultrusion resin polymerization, mathematical simulation of pultrusion cure kinetics, and to study the effect of additives on the simulation of pultrusion production.

To do this, we prepared the pultrusion resin Atlac 430 with set of technological additives, studied their cure kinetics, and described using several mathematical approaches. A method of model refinement was proposed. After we developed several simulations of pultrusion profile curing with set of technological additives described with different models.

1. Analytical Literature Review

With the development of modern civilization and scientific knowledge, the need for new materials for new fields of technology has increased dramatically. In the current real conditions of the level of technology development, strict requirements are imposed on the development of materials that can be operated at: high temperature and pressure; sharp temperature differences; highly corrosive environments. Materials with high strength combined with moderate weight are required. This formulation of the problem gave rise to the development of "substitute materials" (materials with specified properties) with properties that should be appropriate for each specific application of the material. The novelty is not limited to the development of materials with new properties. The creation of new materials poses challenges for the development of promising production methods – improved processing methods, efficient use of energy in processing and preservation of the environment.

Composite materials have been developing rapidly over the past thirty years. The volume and number of applications of composite materials is steadily growing and gaining new markets. Modern composite materials make up a significant part of the market for substitute materials, covering everyday products and the most complex areas of technology.

1.1. Composite materials

Composite materials are usually referred to as materials obtained by combining several materials to obtain properties that cannot be obtained in the source materials. Composite materials consist of two or more physically separable components: matrices[2] and reinforcing filler[3].

Composite materials are classified according to matrix type, the structure and the material of the reinforcing substance. The material characteristics depend on the choice of the initial composite components. The matrix can be thermosetting or thermoplastic, depending on the desired properties of the composite. The structure of the reinforcing material (filler) can be random, unidirectional or laid in a special way. Various fibers are often used as fillers: glass, carbon or basalt.

The main advantage of composite materials over classical ones is the ability to combine different types of matrix and filler for specific tasks. Many composite materials have a high strength-to-weight ratio, chemical resistance, poor thermal conductivity, and are easy to mold.

Thanks to a set of these properties, composite materials have found applications in the aerospace industry: for example, the tail of the Airbus a350. The use of composites in the bodies of F1 racing cars or in the production of prosthetics is widespread. Polymer composites based on carbon fiber can be found in everyday life, for example, they are used in the manufacture of new-generation vacuum cleaners or tires for cars.

<div align="center">a   b</div>
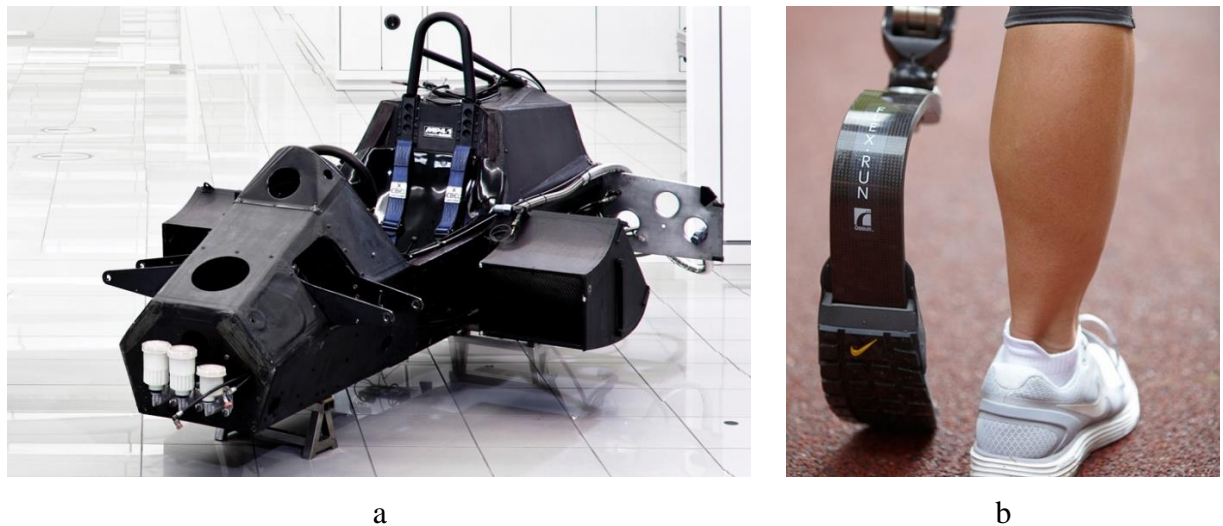
Figure 1. Examples of using composite materials: cocoon of F1 car (a) and the prosthesis (b).

Different manufacturing processes are used to create composite products of different types. Molding is used as an alternative to metal stamping, which allows mass production of composite parts on a prepared matrix. In the production of products by this method, the fiber impregnated with a binder is pressed against the matrix by a press.

Vacuum infusion (Resin Infusion Moulding) allows to create products of complex shapes. In the production of this method, the fiber is pressed to the base (matrix) with a special bag, from which air is pumped out, so atmospheric pressure is used. Then the resin is passed through the fiber and the matrix is heated.

To create more durable composites, the autoclave method is used. The technique differs from vacuum resin infusion by using an additional pressure in an autoclave. The autoclave method is used to produce aircraft parts. The disadvantage of the autoclave molding method is that it is more expensive, requires manual labor, and therefore is not suitable for mass production of products.

Filament Winding is used in the manufacture of rotating bodies: fiberglass pipes for oil and gas, chemical industry, gas-draining fiberglass pipes, fiberglass tanks for storage and transportation of chemically active products, water, fuel and lubricants. The CNC controlled machine wraps the polymer-impregnated fiber layer by layer on a rotating base.
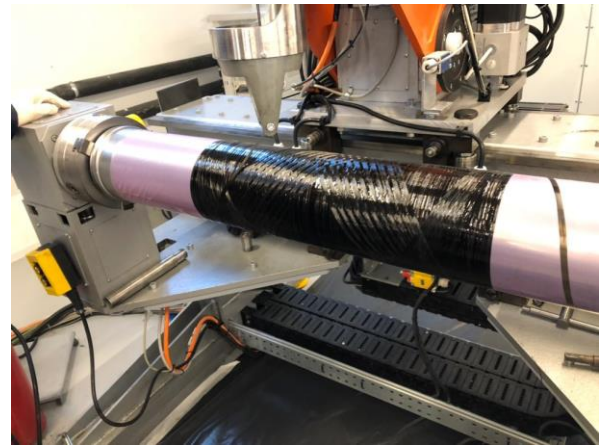
<center>a   b</center>

Figure 2.Manufacturing methods of composite products Autoclave (a), Filament winding (b).

To create products of constant cross-section, pultrusion is used. The rest of the work is devoted to this process.

Pultrusion is the process of producing composite profiles by pulling a resin-impregnated reinforcing fiber through a heated forming die. As a result, the output is a reinforced fiberglass profile, the configuration of which repeats the shape of the die. Using the pultrusion method, it is possible to produce fiberglass products with any profile (fiberglass rod, fiberglass pipe, corner, plate, channel, box, etc.). the production of fiberglass profiles in this way is carried out using a special pultrusion machine.

1.2. Pultrusion background

The history of pultrusion begins when in 1944, J. H. Watson filed a patent for a pultrusion device. Six years later, in 1950, M. J. Meek also applied for a patent. In 1967, the first company was founded – «Glastrusions Inc., » which was engaged in the commercial production of composite pultrusion profile. Since then, more than half a hundred years continuous attempts were made to optimize the production process. The significant number of researches concentrated on the process design in contrast to quality and economic process optimization.

Pultrusion production is a complex technological process. Figure 3 presents the pultrusion unit scheme. The production process follows: the fiber (1) fed through preforming guides(2), where it gets a preliminary form of the future product. Then it passes through the resin bath(3), from there into the heated die(4), and the already rejected formed composite product moves through the pulling device(5) to the cutting saw(6), where the polymerized product is cut to its final length(7). After that, almost done products usually sent for final curing by an infrared heater.
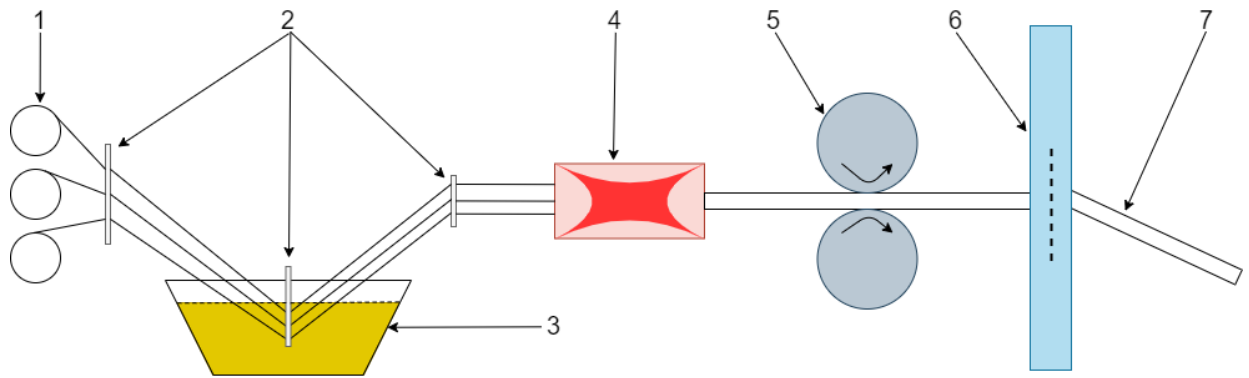
Figure 3. Pultrusion unit: 1- fiber, 2 - preforming guides, 3- resin bath, 4 – heated die ,5 – pulling device, 6 – cutting machine, 7 – produced item.

The main points of pultrusion are described in the following books [4]–[7] and papers[8]–[10]. As mentioned above, pultrusion produces composite products of constant cross-section. Pultrusion allows the use of both thermosetting and thermoplastic binders. The reinforcing material is a directed material from rolls, it could be: glass fiber, carbon fiber or basalt. The field of application of pultrusion composites is wide - some of the significant composite markets include automobiles, rail transport, and the aerospace industry.

| a | b |

Figure 4. Pultrusion profiles by manufacturers Floteck (a), Pulwell (b).

Polymer composites have advantages that traditional materials do not have, such as: resistance to corrosion [11]–[13]. Computational methods and production efficiency of composites in road bridge structures contribute to their wider implementation in various fields of civil engineering. High strength-to-weight ratios in composites reduce the costs associated with using heavy equipment. Composites significantly reduce the cost of maintenance and repair of products due to the good resistance of the material to corrosion and fatigue. It is established that the endurance of the composites has a positive effect on the duration of the product life cycle and extends it.

Of great importance is the possibility of using composite materials in the design and manufacture of bridge coverings[14]–[17]. Sections of pavement made up of hexagonal profiles or double trapezoidal profiles relate to high-strength adhesive under controlled conditions. Composite bridge coverings replace damaged concrete and wood coverings, while their lower weight makes it easier and faster to install them. Bridge coverings are assembled from pultrusion elements that are bonded and glued together. Such coatings consist of a composite double trapezoidal shape that are connected to the hexagons on the bottom that provides mechanical interlock and an extensive bonding surface. The construction of bridges on motorways using composite coatings involves predicting the behavior of this coating under the influence of loads from traffic participants. Traffic loads create repeated stress cycles on the pavement during the lifetime of the structure. Composite bridge coverings of modular construction are made of a long length due to the technological process used (pultrusion technology), and then cut to the size required by the customer. Due to this, considerable flexibility is achieved in the manufacture of composite bridge coverings of various sizes.

An outstanding field of application is bridge construction. The high strength-to-weight ratio of the pultrusion composite[18], [19], made it possible to significantly lighten the weight of the entire structure, and therefore reduce the load on the load-bearing supports. This property of composites allows them to replace traditional materials in this field[20], [21].

Composites proved to be very convenient for repairing, upgrading and improving concrete bridges in order to extend the life of existing structures. The commercial value of such repairs has been confirmed by hundreds of examples[20]. in Europe, Japan, and North America. In recent years, the practice of manufacturing bridges with spans and gangways made entirely of composite materials has been expanding [22]–[24] Examples of such bridges are also available in Russia (pedestrian bridges over railway tracks at Chertanovo and Kosino stations, and pedestrian Park bridge in Moscow). Dubna of the Moscow region-manufacturer of LLC NPP APATECH, Moscow).

a   b

Figure 5. Pedestrian bridges over railway tracks at Chertanovo (a) and Kosino(b) stations.

Strongwell makes bridges with composite load bearing structures [25]. The design elements are pultrusion profiles. Pultrusion composite bridge elements withstand critical mechanical stress at a much lower weight than steel. As a result the span of such a truss is easily installed without heavy equipment and a large number of workers

Figure 6. Pultruded bridges with composite load-bearing structure manufactured by Strongwell.

As mentioned above, pultrusion production is always a balance between performance and quality of the products produced. As the speed of production increases, the quality of products decreases, and various defects appear: porosity and changes in geometry[7].

a   b

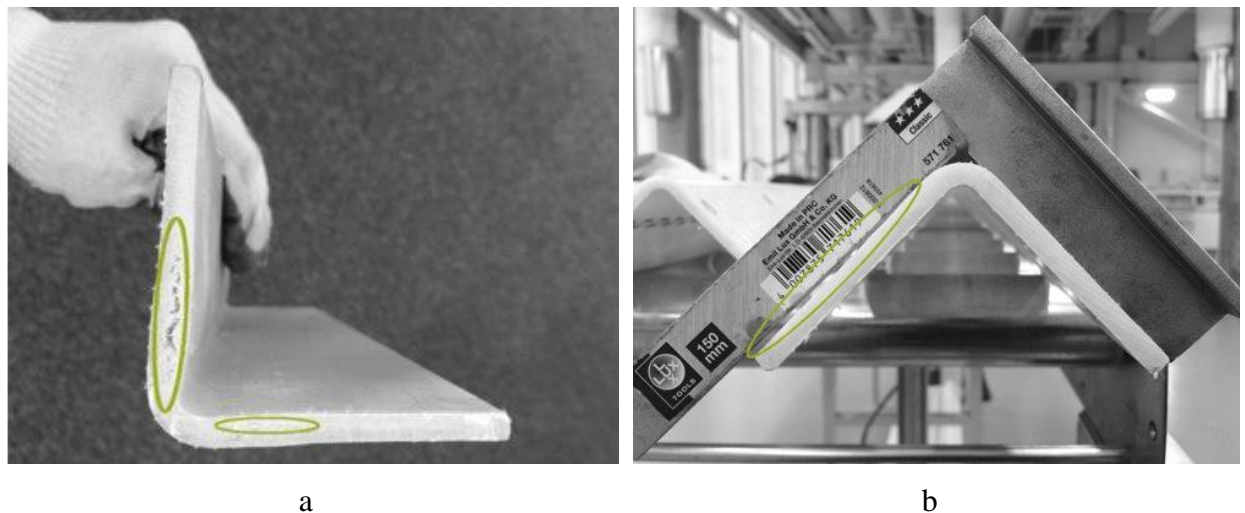Figure 7. Defects crack (a), geometry change (b).

To increase the productivity of the pultrusion machine without causing defects, it is necessary to optimize the production parameters. Due to their large number, the search for optimal parameters by trial and error becomes unnecessarily expensive and long. Therefore, various process modeling techniques are used to optimize pultrusion production.

1.3. Pultrusion simulation

The main task of pultrusion modeling is to optimize production parameters to produce a high-quality composite profile with the highest machine performance. Pultrusion production has many parameters available for optimization, the main ones are the pulling speed, the temperature and geometry of the die, the amount and location of the reinforcing filler, as well as the chemical composition of the binder.

To solve the problem of parameter optimization, mathematical models are built that reflect the influence of these parameters on the quantity of composite profile produced and its quality. These models are based on mathematical representations of the influence of various parameters on the curing process of a composite material. In academia, there is currently a steadily growing trend toward the development of methods of numerical simulation for processes taking place during pultrusion[10][7]

The first works did not consider many physical parameters, such as the thermal conductivity of the material, and were very simple[26]. Gradually, these models were added to the influence of the pulling force by the Batch [27]. Moschiar in [28], [29] improved the Batch model. The new model considered thermal conductivity and pressure changes in the die. Lee and modified these models to a thermoplastic pultrusion composite[30]. To obtain high-quality models, numerical modeling methods are used. Examples of the application of numerical modeling can be seen in the works [2], [31]–[33]

New steps in planning and optimizing pultrusion production are being taken by Carlone. His work presents solutions to the problem of composite curing simulation using a more flexible approach - neural networks, combining the proposed method with the finite element method for the production of autoclave composites [34], [35]. His works showed that using dynamic neural model of the autoclave curing is ab le to predict the temperature peaks inside the composite with complex shape in synergy with different fiber volume fractions.

The properties of the components involved determine the mechanical properties of the manufactured parts. Various models have been proposed for determining the constitutive ratio of FRPs depending on the properties of components and volume proportions [36], [37]. Boghetti and Gillespie developed an analytical model for calculating the mechanical properties of fiber-reinforced plates [38]. They analytically expressed the relationship between the final mechanical properties of the composite and the volume proportions, as well as the properties of each component. One of the main points of this model was to predict the development of the resin during the curing reaction in terms of modulus of elasticity, thermal expansion, and chemical shrinkage. Although this approach was not developed specifically for Pultrusion components, it is well suited for pultrusion modeling. In fact, it was used to model the effect of pultruded process

parameters on final mechanical properties and stresses and elongations caused by the process on pultruded parts[39]–[42].

The actual properties of the material depend on the reinforcement architecture and its orientation [6], [43]. In the scientific literature, there are examples that characterize the traction behaviour of pultruded fiberglass in relation to non-axial loads [44], [45].. Composite elements show much higher performance under external loads parallel to the direction of the fibres. The modulus of elasticity, as well as the size of the final stress, significantly decreases at low angles of inclination, while at angles of inclination above 45°, the modulus changes are insignificant [44]. Some authors have modified the Hankinson formula [46] and calibrated to obtain the tensile σ_θ and elastic modulus E_θ of manufactured parts for each angle of inclination θ depending on the longitudinal direction (σ_0 and E_0) and transverse direction (σ_{90} and E_{90}) prediction properties [45].

In contrast to the case of tension, the compressive elements Pultrude much less. Compression mechanical testing of pultruded structural coupons presents various complex aspects related to fibre alignment, coupon geometry, load input, stress concentration, bending strength, and compression of the end surface of the sample. FRP profiles have high longitudinal strength but low transverse strength [47]. Instead of collapsing due to compression, they are more susceptible to geometric instability, local face compression, or local face roll.

The pressure behaviour of pultruded fiberglass depends on the volume fraction of the fibre, the properties of the raw material used, and the relationship between the matrix and the reinforcement [48], [49]. The compressive strength reaches higher values as the volume fraction of the fibre increases. However, when the proportions of the fibre polymer are excessive, the compressive strength decreases somewhat [48]. In fact, fibre reinforced composite exhibit brittle behaviour with a small number of fibres, which is destroyed due to the propagation of several transverse cracks, while with an excessive number of fibres, the failure occurs mainly due to the longitudinal coupling at the fibre-matrix surface boundary [48]. Compression tests of coupons reinforced with various materials show that glass and carbon fibre exhibit similar behaviour: high strength and brittleness. In contrast, polymers reinforced with Kevlar have a low modulus of elasticity and strength with high plasticity. Subsequent processing of the results of compression tests allowed researchers to indirectly evaluate the compression properties of fibres based on the inverse mixture rule [48].

Due to the structural morphology of pultruded fiberglass, different types of shear behavior occur depending on the direction of the external shear load from the point of view of the reinforcement architecture. The most commonly studied behavior is shifting in the plane and between layers. Various methods of measuring the shear modulus have been described in the scientific literature. The most commonly used methods are the cylinder torsion test [43], the V-shaped recess test (also known as the Josipescu method) [44], [50], [51], [52] Off-Axis test [44],

[53], [54], three-point and four-point bending tests [55], [52]. In addition, Mingini et al beat. In his experimental work, he put forward a new four-point bending machine for determining the traction module and compared it with the traditionally used three - and four-point bending machine [56]. An experimental comparison of the Josipescu method, other than the axial pressure and attempts other than the installation for the tear test, compression plane shear measurements showed that the results from the off-axis pressure and try V-groove tests meet the requirements, while the shear response of the non-axial tear test, compression is low. This behavior is probably related to the stress state during tensile tests, in which micro-cracks and micropores become visible in the glass wool. Therefore, the shear behavior cannot be measured using an off-axis tensile test. However, it should be noted that the shear modules calculated by analyzing the initial linear response from the results of both non-axial tests are very close to each other [44].

An important part of the curing simulation of composites is to model the polymerization of the matrix resin. All considered approaches in their teaching are based on different models of resin polymerization, but it is the model of resin curing in the production of a pultruded profile that is the cornerstone of the simulation.

1.4. Cure kinetics

Polymers are materials consisting of long repeating chains of molecules. They have unique properties depending on the type of molecules being joined and how they are connected[2]. Some of them bend and stretch, such as rubber and polyester. Others are hard and rigid, such as epoxides and organic glass. The term "polymer" is usually used to describe plastics that are synthetic polymers. However, natural polymers also exist for example, rubber and wood are natural polymers consisting of a simple hydrocarbon, isoprene. Proteins are also natural polymers, made up of amino acids.

Baran in his models pays more attention to the influence of the cure degree on the profile characteristics during production. He focused on thermo-chemical and mechanical analyses of the pultrusion in which process-induced stresses and distortions, together with thermal and cure developments, are addressed[57].

Equations that determine the degree of resin polymerization are a presence in all the papers above. This dissertation also based on Magnus's research[58] and Baran's article[59]. For the most part of papers, authors use the extended Prout-Tompkins equation. To determine the kinetic constants of the model, differential scanning calorimetry is used. In this paper, authors used a DSC to collect data for vinyl-ether resin curing simulation.

Adding a hardener and applying heat to it starts the reaction, the resin polymerizes releasing additional heat. Increasing heat accelerates the rate of polymerization. The faster the

polymerization, the faster the heat release begins. As a result of these processes, the resin boils and instantly hardens.

The history of thermosetting resin, and it is chemical analysis carried out well with this work [60]. To describe it briefly: the long resin oligomers have weak bonds or free radicals at both ends. The hardener connects to oligomers via free radicals or replaces weak bonds in molecules. In this case, one molecule of the curing agent relates to several molecules of a resin, stitching them together. Figure 8 shows the structure of a widely used thermosetting cured resin-cured epoxy glue. The hardener thiamine is shown in dotted lines and red, while the resin is shown in black. The epoxy groups of the resin have reacted with the hardener and are no longer present in the primary form. The material is highly dry and contains many OH groups that give adhesion properties.
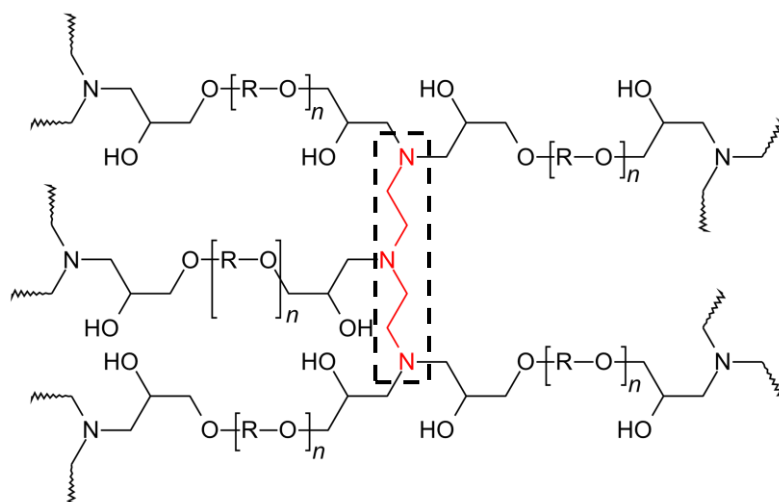
Figure 8. Cured epoxy glue structure.

As mentioned above, thermosetting resins generate heat during polymerization. This means that by capturing the generated heat, we can describe the polymerization process. To do this, use the method of differential scanning calorimetry.

1.5. Differential scanning calorimetry

The technique was developed by E. S. Watson and M. J. O'Neill in 1962 and introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. The first adiabatic differential scanning calorimeter that could be used in biochemistry was developed by P. L. Privalov and D. R. Monaselidze in 1964 at the Institute of Physics in Tbilisi, Georgia. The term DSC was coined to describe this instrument, which measures energy directly and allows precise measurements of heat capacity. The use of thermal analysis to describe the polymerization of resins for composites has become very popular these days, and

international measurement standards have been developed[61]. Unified experiments that meet the standards allow scientists to compare the kinetics of resin polymerization with each other.

Differential Scanning Calorimetry is a method based on recording the difference in heat fluxes depending on temperature and time, which allows studying thermal processes, identifying or comparing materials. The principle of operation of the DSC is as follows: 2 pans are installed in the cell: with a sample and a reference one. The reference pan is usually empty or with a sample in which kinetic parameters are known in advance. An inert gas is pumped in a cell, usually argon or nitrogen, and the cell is heated up. The DSC signal represents the temperature difference between the reference pan and the pan with the measured sample[62]. The full Principe of DSC is described in the following works: [63], [64].

Thermosetting resin generates heat during polymerization. The calorimeter picks up this heat. By describing the amount of heat released at different temperatures, we can qualitatively describe the kinetics of resin polymerization.

The mass of the set sample is between 5 and 10 milligrams. The small mass of samples allows to neutralize the effects that the thermal conductivity of the material makes, and it is assumed that the temperature of the sample is uniform. To determine the kinetic parameters of resins, scientists usually use several scans of the resin at different heating rates. In the instructions for DSC, it is recommended to use heating rates that differ by 2 times: for example, 3, 6, and 12 Kelvins per minute. However, Baran's research is based on heating rates of 5, 7.5, and 10.

Differential scanning calorimetry is widely used today. It is used to describe the properties of not only thermosetting resins. This method allows to find out the heat capacity of materials, see the glass transition, find out the melting and boiling points of materials.

The device consists of a cell in which researchers install two pans. One pan contains the test material, the other is empty. An empty pan serves as a sample and allows us to observe only the material without interference. The mass of the test material varies from 5 to 10 milligrams. This small mass allows the calorimeter to remove all the generated heat from the closed system. Also, the small mass of samples ensures uniform heating and eliminates the effects that heat capacity can introduce. The sample is placed in a pan and sealed with a lid. A small hole in the lid of the pan is made to remove the pressure generated by the heated air. After installing both pans in the seats, the cell is closed.

After that, scanning starts: the cell temperature equalizes at the set start temperature, and an inert gas is pumped into the DSC cell: usually, nitrogen or argon is used. After that, the DSC heats the cell according to the set temperature program. The sensor compares the temperatures of both pans across the entire temperature program, and the computer records data from this sensor. According to the studied articles, for unambiguous determination of the kinetic parameters of

thermosetting resin, three measurements are made at heating rates of 5, 7.5 and 10 Kelvins per minute. After all measurements are made, the data is have to be processed.
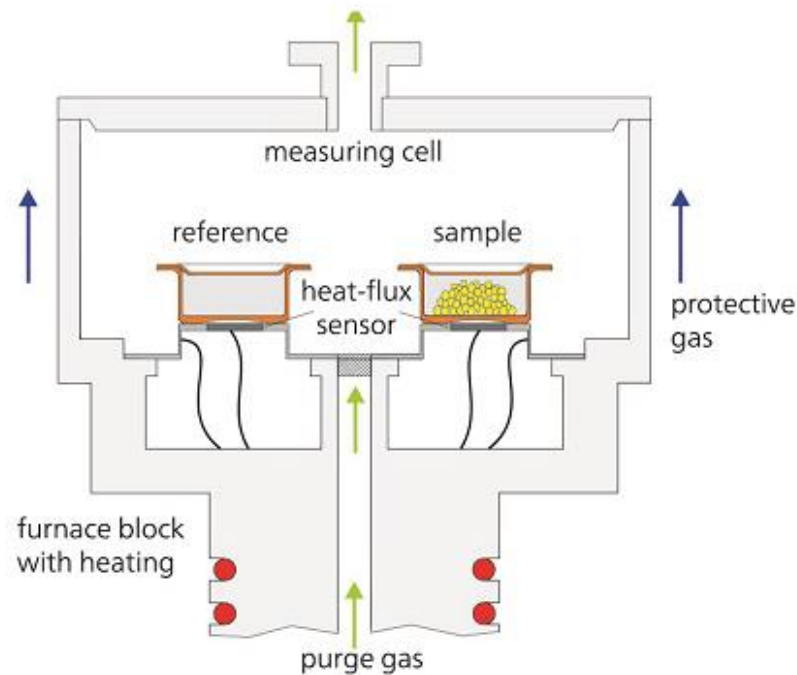
Figure 9. The DSC cell.

1.6. Data preprocessing

Data processing and primary analysis allow partial characterization of the resin. Already at this stage, we can see the temperature and time of the beginning and end of the reaction. We can also see the moment when the reaction was most rapid - the peak of polymerization.

First, the technician sets the start and endpoints of the reaction: in figure 3.1, these are points A and B. the Program calculates the tangent to the signal at these points. The program also finds tangents at the inflection points of the signal. The intersections of these tangents are offset and endpoints. The baseline is also built; it simulates a zero-signal considering the phase transition of the material's heat capacity. During the curing process, the resin increases its heat capacity, so the right shoulder of the graph is higher than the left. After finding the baseline, the algorithm calculates the area of the enthalpy peak, considering the baseline. In figure 10, the area under line is colored blue. The peak area is the amount of heat released by the resin during polymerization reduced to the mass of the test specimen.

Figure 10. DSC signal preprocessing.

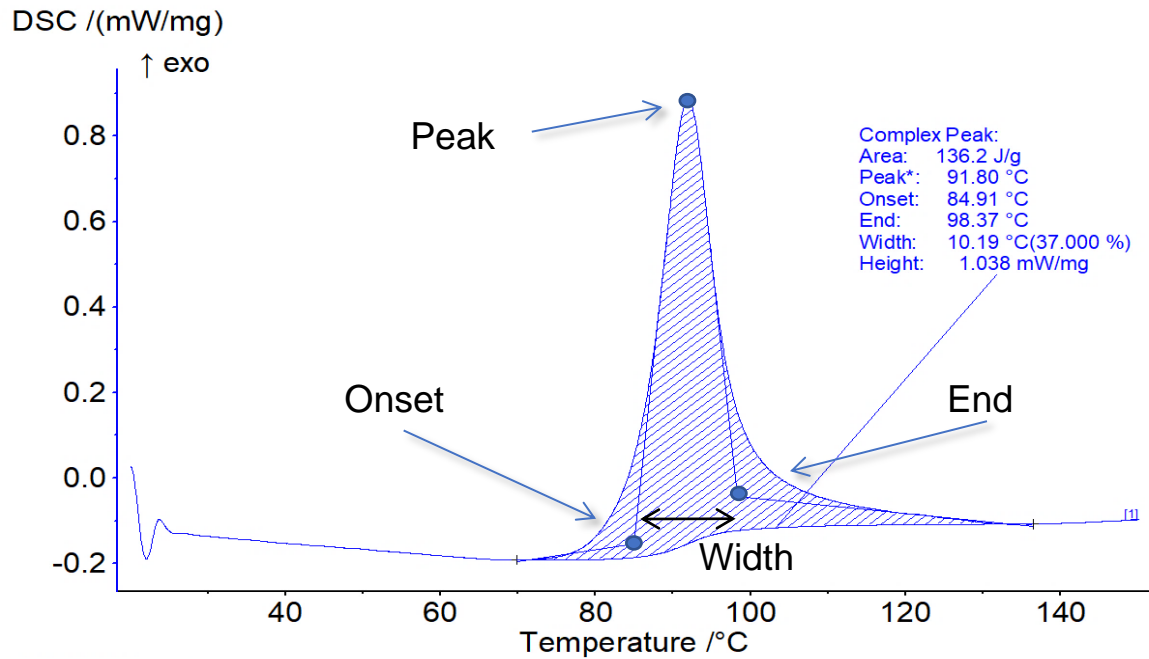The parameters found: the start, maximum, and peak points of polymerization are unique for each resin. The peak area is also unique. Also, changing the resin mixture formulation changes these parameters. This is followed by processing of the received data for cure simulating.

1.7. Resin cure kinetics simulation

The application of kinetic analysis will be considered under two aspects. From the scientific aspect, an attempt will be made to record the individual steps of the entire process as a model to clarify them and interpret them in a physical/chemical sense. From the technical aspect, the kinetic analysis will be examined as a tool for data reduction. The information will be extracted from a series of measurements with many data points in the form of a model with few parameters. This model will then serve in the preparation of predictions and for process optimization.

Considering the application of kinetic analysis under these two aspects requires a different procedure: Under the scientific aspect, a model (hypothesis) is set up, in which the individual reaction steps can be interpreted chemically and/or physically. The hypothesis is compared with the experimental results and, if possible, with results obtained from other experimental methods as well. If the hypothesis and experiment are contradictory, the hypothesis is replaced with further experiments can be carried out in order to further support or refine the hypothesis[65].

In many cases, the tests involve variation of the test piece, to make its specific properties apparent. Such a procedure for thermoanalytical measurements is demonstrated by Flammersheim,

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et al[66]. Under the scientific aspect, the analysis of the reaction kinetics should, therefore, answer three questions:

1. How does one investigate the mechanism of the gross reaction?
2. How does one calculate the degree of conversion as a function of time?
3. How can one make the course of an elementary reaction understandable with molecular models?

Under the technical aspect, one usually starts with a given test piece. A targeted variation of this sample is often impossible since, for example, the supplier of the material does not want to reveal his know-how. The kinetic model is, to the greatest extent, formally. Therefore, the reactants are also formally; their concentrations assume only values between 0 and 1. The kinetic model, as a combination of individual reaction steps, serves as an efficient filter for data reduction. An interpretation of the single steps and their parameters is not planned for the time being[67]. Often, the behaviour of the test piece is investigated under conditions as close as possible to those for which the predictions must be made. In contrast, the effects of specific conditions[68] are only seldom taken into consideration. The simplest model to design should be capable of describing the essential characteristics of the data in the reaction field over the time and temperature of the measurements.

A basic statement in statistics says that the level of confidence of predictions in the range of analysis is especially high and is directly proportional to the quality of the fit. For thermoanalytical measurements, this means that the largest possible range of the accessible time/temperature field[69] must be covered with isothermal measurements at different temperatures or with dynamic measurements at different heating rates. In their practical realization, the two aspects have much in common, despite their antithetic goals:

•·A kinetic model must be set up. The kinetic model contains, on the one hand, the reaction diagram, i.e. the combination of single reaction steps, and on the other hand, the assignment of each reaction step to a reaction type. The parameters of the model must be specified such that the experiment is described as well as possible.

•The aim is a comprehensive solution, which is valid for a more excellent range of test parameters.

All these approaches to modelling chemical processes have been proposed since 1970 and are actively used today. To get acquainted with all the models the authors used the Netzsch thermal analysis documentation[70]. It describes more than 15 equations for modelling all thermodynamic processes and instructions for calculating kinetic constants. The above-stated requirement, for the most comprehensive validity possible of the solution found, is solved in a series of papers [71]–[73], in that first of all each measurement in a series of measurements is individually analyzed and only one-step reaction processes are considered. Only in a second step is a compromise solution sought by averaging the calculated kinetic parameters.

Returning to the topic of pultrusion, Prout Tompkins and Nth order model with autocatalysis are used to model the polymerization of composite resins[74]–[76]

By the nature of heat release by the resin during polymerization, it is possible to describe the course of its curing. The resin cure degree at each time is calculated as the ratio of the heat released to the total amount of heat released, according to formula 1.

$$a(t) = \frac{H(t)}{H_{total}} \tag{1}$$

Where: $H(t)$ - current amount of exothermal heat, H_{total} - total exothermal heat, $a(t)$ - resin cure degree. In this way, we get the degree of resin polymerization at each time. In addition, we know what the temperature in the DSC cell was at that time.

Resin cure kinetics simulation means building a mathematical model that will predict the resin cure rate(2), based on some factors. Typically, in classic models, the alpha gain is modeled based on the current resin temperature and degree of current resin polymerization. There are also other methods that are based on all previous indicators of temperature, degree of polymerization, and curing rates.

$$\frac{d\alpha}{dt} = \frac{a_i - a_{i-1}}{t_i - t_{i-1}} \tag{2}$$

Thus, by calculating the curing rate degree at moment of time under different conditions, we can set these conditions and calculate the degree of polymerization as the sum of its increments. Equation (3) presence the calculation of the resin cure degree at each time to stimulate the curing of the resin process.

$$a(t_k) = a(t_{k-1}) + \frac{da_k}{dt_k} \tag{3}$$

Since equation (3) is valid for calculating the degree of curing of the resin over the entire time period, this equation can be reduced to the form (4)

$$a(t_k) = \sum_{i=0}^{k} \frac{da_i}{dt_i} \tag{4}$$

According to this equation, the curing simulation is performed step by step. For the calculation it only remains to find the calculation method of $\frac{da}{dt}$ in different conditions. Next, we will consider methods for calculating the resin curing rate degree.

As mentioned earlier, models simulating the degree of resin polymerization depend primarily on two factors: the current temperature and the current degree of polymerization. Therefore, mathematical models take the form (5)

$$\frac{da}{dt} = k(T)f(a) \tag{5}$$

Where:

da/dt – curing rate (min-1);

k(T) – reaction rate constant at temperature T (min-1);

f(a) – function associated with the reaction type (conversion function).

The generally accepted equation for simulating reaction rate constant at temperature T is the Arrhenius equation(6).

$$k(T) = Ae^{-\frac{E}{RT}}$$

(6)

Where:

A – preexponential factor (min^{-1});

E – activation energy(J·mole^{-1});

T – absolute temperature (K);

R – universal gas constant equal to 8,314 (J·mole^{-}·K^{-1}).

For determination of kinetic parameters: activation energy, preexponential factor, and reaction order – by values of the heat flow and total heat of reaction used model representations of reactions of nth order or autocatalytic reactions. The most popular equations are presented in table 4.1. it is essential to notice that all of them have a part with the Arrhenius equation.

Table 1. Most popular equations for cure kinetics simulation.

Model name	Model equation	Reference
Reaction of n-th order with autocatalysis	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n(1 + K_{cat} * \alpha)$	(7)
Reaction of first order with autocatalysis	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)(1 + K_{cat} * \alpha)$	(8)
Expanded Prout Tompkins equation	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n\alpha^m$	(9)

Let us consider the search for kinetic constants using the example of the expanded Prout Tompkins equation (9). Kinetic constants are describing the polymerization of the resin. Where n is educts coefficient and m is product coefficient.

The search for kinetic constants is performed using multiple linear regression analysis. The mathematical apparatus for searching for regression coefficients is described in following books[77]–[79] and articles[30], [59]. Use this method needs the equation in the form (10):

$$y = ax_1 + bx_2 + cx_3 + dx_4$$

(10)

The most straightforward and most widely used approach to bring equations to a multilinear form is to logarithm equation (9). Then equation (9) will take the form (11).

$$\ln\left(\frac{da}{dt}\right) = \ln(A) + \left(-\frac{E_a}{RT}\right) + n(1-a) + ma$$

(11)

Where $\frac{da}{dt}$ is the curing rate which calculates with equation (2), R is universal gas constant equal to 8.314, T is the current absolute temperature at moment t which obtains from DSC, a is the current cure degree calculates with equation(1), this coefficient proportional to the reaction product, $1 - a$ is a coefficient proportional to the amount of the source substance. The cure kinetics equation could be performed in the standard form of multiple linear regression (12).

$$y = x_1 + x_2 \left(\frac{-1}{RT}\right) + x_3(1 - a) + x_4 a \tag{12}$$

Where x_1 is log(A), x_2 is activation energy (Ea), x_3 is educts coefficient (n), and x_4 is products coefficient (m).

Thus, researchers calculate the kinetic constants of the resin, and characterize it. After these calculations, a simulation of resin curing could be performed. The models used are universal for various methods of manufacturing composite materials, if you neglect the various factors that change the kinetics of the resin. One of these factors is the technological additives used in pultrusion.

1.8. Features of pultruded resins cure kinetics

While working on the thesis, we noticed that the addition of additives necessary for pultrusion changes the kinetics of resin polymerization. Primarily was studied the effect of zinc-stearate and aluminum hydroxide. A literary review has shown that this is a common occurrence. There are some papers considering the effect of additives on resin polymerization.

Dilmurat Abliz, in his work[80] studies the effect of particles of boehmite (AlOOH) on the epoxy resin curing and shows a visible difference in kinetics. Mehdi Ghaffari does the same[81] for zinc oxide and shows a significant effect of particles on the cross-linking of resin molecules. However, a literature search did not show any articles on the effects of additives used in pultrusion. In addition, epoxy resin is considered everywhere. But in pultrusion production, vinyl-ether is more often used. It is cheaper but requires additional precautions: a respirator and glasses.

1.9. Goals & objectives

Based on provided literature survey of pultrusion process, the object of research, the main goal and objectives of this work are follows. The object of this research is the curing of pultrusion vinyl-ether resin. The goal is to evaluate the effect of additives on the pultrusion production simulation results and to refine the mathematical description of resin curing kinetics.

To achieve this goal, the following tasks were identified:
1. Manufacture pultrusion resin in accordance with the industrial recipe with different presence of technological additives.

2. Perform measurements of manufactured resins curing with differential scanning calorimetry.

3. Evaluate additives effect on onset, peak and end points of DSC signal. As well as evaluate changes in the signal peak under the influence of additives.

4. Describe the kinetics of resins with different additives. And choose the best method to simulate vinyl ester curing

5. Simulation of pultrusion production based on calculated mathematical models.

2. Materials and Methods

This Chapter is dedicated to experimental work carried out to characterize an industrial vinyl ester resin prepared for the pultrusion process. Pultrusion resin has technological additives, so a set of resins in four containers was prepared to study their effect. Then all the resins were subjected to DSC scans. Several classical models were used to simulate resin polymerization. Machine learning and neural network approaches were also used for simulating.

2.1. Materials description

The following materials were used in this work:

- Atlac 430 – vinyl ester resin;

- Trigonox C - Initiator for (co)polymerization of ethylene, styrene, acrylonitrile, acrylates, and methacrylates;

- Perkadox 16 - initiator for suspension polymerization of acrylates and methacrylates;

- BYK-A555 – Deaerator;

- BYK-W996 - Wetting and dispersing additive;

- Aluminum hydroxide - Burning preventor;

- Zinc stearate - Friction reducing additive.

Atlac 430 is an epoxy bisphenol A vinyl ester, dissolved in styrene. Atlac 430 can be used in all fabrication methods but is especially adapted to meet the requirements of filament winding, centrifugal casting, hand lay-up and spray-up applications. Atlac 430 provides resistance to a wide range of acids, alkali, and bleaches for the use in corrosive environments in the chemical processing industry. The favorable combination of thermal resistance and elongation makes this resin suitable for applications exposed to intermittent temperatures.

Table 2. Properties of cast unfilled Atlac 430 resin.

Property	Value	Unit	TM
Density, 20°C	1145	kg/m3	-
Tensile strength Mod.	95	Mpa	ISO 527-2
Mod. of elasticity in tension	3.6	Gpa	ISO 527-2
Elongation at break Flexural	6.1	%	ISO 527-2
Flexural strength Mod.	150	Mpa	ISO 178
Mod. of elasticity in bend	3.4	Gpa	ISO 178
Elongation in flex	6.5	%	ISO 178
Impact res. - unnotched sp.	28	kJ/m²	ISO 179
Heat deflection temp. (HDT)	105	°C	ISO 75-A
Glass transition temp. (Tg)	130	°C	DIN 53445

The manufacturer recommends using the following conditions for curing the resin. "Cured with 1 ml Butanox LPT-IN (AKZO-Nobel) and 0.5 ml Co-octoate solution (1 % Co in styrene) added

to 100 g resin. For HDT and Tgdyn post-curing 24 h at 120°C"[82]. In the laboratory, the Atlac 430 is stored in a 200 liters aluminum barrel under normal conditions. Before making the mixture, the barrel was shaken on a special bracket.

Trigonox C is a tert-Butyl perobenzoate. It is used as initiator for (co)polymerization of ethylene, styrene, acrylonitrile, acrylates and methacrylates, provided by Akzo Nobel Polymer Chemicals. CAS number – 614-45-9, EINECS/ELINCS number - 210-382-2.
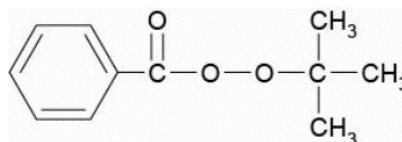

Figure 11. Tert-Butyl perobenzoate formula.

Trigonox C is a light-yellow transparent liquid. Physical properties under normal conditions (20 degrees) density 1.04 g/cm3, Viscosity - 6.5 mPa.s. Polymerization of styrene Trigonox C may be used for the (co)polymerization of styrene in the temperature range of 100-140°C. In practice, combinations of two or more peroxides with diverging activities are used to reduce the residual monomer content in the final polymer and to increase reactor efficiency. In suspension polymerization processes Trigonox C is often used for reduction of residual styrene content during the final polymerization stage[83]. In the laboratory, Trigonox C is stored in a dense plastic bottle in a metal Cabinet, protected from sunlight.

Perkadox 16 is a Di(4-tert-butylcyclohexyl) peroxydicarbonate. Used as initiator for suspension polymerization of acrylates and methacrylates. CAS number – 15520-11-3, EINECS/ELINCS number - 239-557-1.
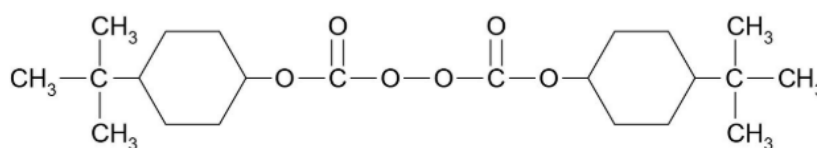

Figure 12. Di(4-tert-butylcyclohexyl) peroxydicarbonate formula.

Perkadox 16 is supplied as a white powder. Bulk density in normal conditions - 450-480 kg/m³. Thermoset curing agent: Perkadox 16 is a solid peroxydicarbonate which is used for the curing of unsaturated polyester resins and methacrylic resins mainly in the temperature range of 60°C and higher. Thermoset curing agent: Perkadox 16 is a solid peroxydicarbonate which is used for the curing of unsaturated polyester resins and methacrylic resins mainly in the temperature range of 60°C and higher[84]. Perkadox 16 requires special protection from moisture, so the powder is stored in a series of closed plastic bags in the laboratory in the laboratory Cabinet and

is not affected by sunlight. Perkadox 16 is poorly soluble in resin, so when it was added to a common barrel with the mixture, a paste-like substance based on Perkadox 16 and Atlac 430 was first made. All the following substances are processing AIDS and do not participate in the polymerization process of the resin.

BYK-A555 Silicone-free polymer-based air release additive for unsaturated polyester resins. Suitable for all types of unsaturated polyester resins and processing methods. Also suitable for pultrusion applications with acrylic, unsaturated polyester and vinyl ester resins. Properties: density (20 °C) - 0.88 g/ml, refractive index (20 °C) - 1.507, flash point - 43 °C, hazen color number less than 250, turbidity less than 10 TE/F[85]

BYK-W996 is wetting and dispersing additive for filled, unsaturated polyester systems and epoxy systems. BYK-W996 composition is a solution of a copolymer with acidic groups. Properties: Acid value - 53 mg KOH/g, density (20 °C) - 1.03 g/ml, refractive index (20 °C) - 1.462, water content less than 0.13 %, flash point - 42 °C[86]. BYK-W996 as well as BYK-A555 is produced by "BYK additives & instruments". Both BYK production additives appearance as liquids and are stored in plastic bottles under normal conditions in a dark laboratory Cabinet.

Aluminum hydroxide is burning preventor. White powder delivered in paper 25 kg bags CAS No.: 21645-51-2. Aluminum hydroxide is decomposes under high temperature, releasing water(13). This unique property allows the use of aluminum hydroxide to prevent burning of the composite material.

$$2Al(OH)_3 \xrightarrow{t>575^oC} Al_2O_3 + 3H_2O \tag{13}$$
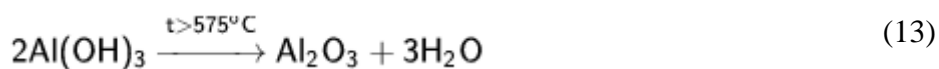
One of the main uses of aluminum hydroxide is as a raw material for the manufacture of a compound of other aluminum: alumina special aluminum, aluminum sulfate, polyaluminum chloride, aluminum chloride, zeolites, sodium aluminate, activated alumina and aluminum nitrate . A form of aluminum hydroxide that is deposited using new gel, which is the basis for the use of aluminum salts as flocculants in water treatment. This gel crystallizes over time. Aluminum hydroxide gels can be dehydrated (for example: using an aqueous solvent insoluble in water such as ethanol) to form an amorphous ammonia hydroxide powder that is soluble in acids. Aluminum hydroxide powder that has been heated to a high temperature under conditions that are carefully controlled is known as activated alumina and is used as a desiccant , as an adsorbent in gas purification, as a support catalyst Claus for water purification, and as an absorbent for the catalyst during the manufacture of SCLAIRTECH polyethylene. Aluminum hydroxide does not require special storage conditions and is stored in a covered paper delivery bag.

Zinc- stearate is friction reducing additive. Another name – Zinc soap: it's white light crystalline powder, insoluble in water, cold ethanol and ether, soluble in hot benzene, toluene and turpentine, slightly soluble in hot ethanol and ether. It is used in the manufacture of PVC compositions as a temperature stabilizer. Levelling agent in polyurethane and nitrocellulose

lacquers, injection mold lubricant for plastics processing, anti-blocking lubricant in the production of rubbers. In the production of cosmetics, it is used in dense powders, improves the adhesion and coating of powders. Sealing lubricant in ester impregnations for sheet forming materials, glass-filled premixes, etc. Water repellent agent and lubricant for coatings and various structures. Increases resistance to sulfur staining, used as a non-stick agent, used as a vulcanization activator and plasticizer (rubber industry). It is used as a plasticizer and activator for vulcanization of rubbers and rubber mixtures. It is recommended to produce transparent rubbers, used as a duster to prevent sticking of rubber products and mixtures, and used as an anti-blocking lubricant in the production of rubbers.

In pultrusion, the use of zinc stearate is necessary to provide the composite sliding inside the die: zinc stearate forms a thin film between the resin and the die, preventing the resin from sticking to the heated die. Zinc stearate forms a thin film between the resin and the die, preventing the resin from sticking to the heated film. Thus, zinc stearate ensures sliding and reduces loading on the pulling device. Thus, zinc stearate reduces the load on the pulling device and increases the service life of the pultrusion unit.

2.2. Resin mixture

To conduct the measurements, a base mixture was first created with a resin, a hardener, and a pair of technological additives that ensure the quality of the mixture. After that, the base was poured into containers and additives were added to each container in according figure 13.
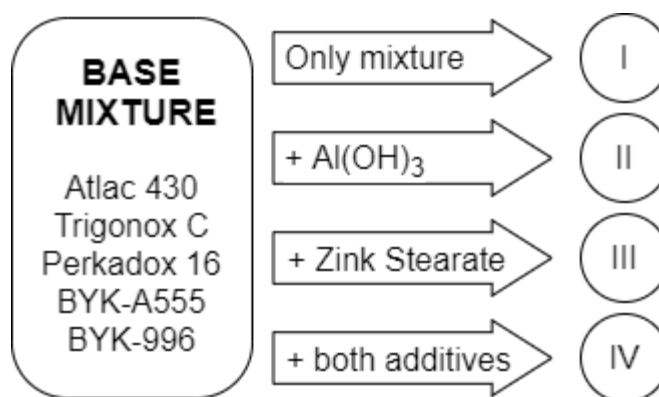

Figure 13. Mixture structure in the containers.

Mixing of the base took place in a 50-liter metal bucket mounted on a floor scale. The first component was vinyl ester resin Atlas 430, it was shaken on a metal bracket and poured into a metal bucket 25.07 kilograms. Then 90 grams of deaerator BYK-A555, 180 grams of wetting additive BYK-W996 and 380 grams of harder Trigonox C were poured into it. The mixture was mixed with an industrial mixer in the same metal bucket for 1 minute.
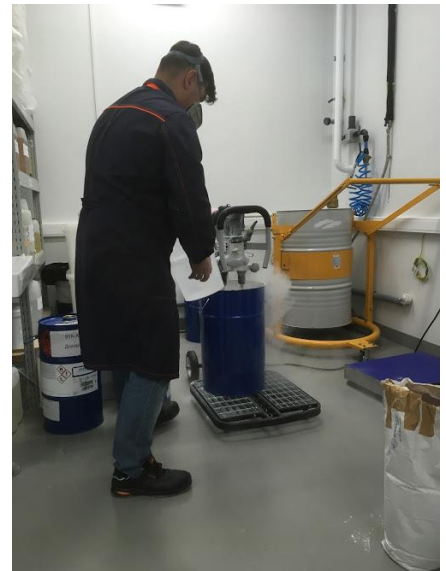
Figure 14. Mixture preparation: barrel with Atlac 430 on the bracket (a), mixing in a 50 liter bucket with an industrial mixer (b).

To add hardener Perkadox 16, 100 grams of the mixture was removed from a metal bucket and placed in a plastic container. Perkadox 16 powder was added to this container and thoroughly mixed. This operation resulted in a white paste. For more thorough mixing, the paste was moved to a cutting board and crushed the remaining Perkadox 16 grains with a metal spatula. The resulting homogeneous paste was mixed into the overall mixture using a mixer. After conducting these procedures, we produced the base mix.

Then base mix was poured 100 milligrams into 4 disposable plastic containers with lids. Container 1 hold only the base mixture. 31 grams of aluminum hydroxide was added to container 2. 4 grams of zinc stearate were added to container 3. 31 grams of aluminum hydroxide and 4 grams of zinc stearate were added to container 4. All the resulting mixtures were carefully mixed with individual wooden spatulas, marked and closed. To follow the recipe, we used ordinary laboratory scales with a maximum permissible weight of 200 grams and an error of 0.01 grams.

Figure 15. Perkadox 16 paste (a), packaging base mixture by containers (b).

The mixing of the resin components was perfectly according to the industrial recipe. Both hardeners balance each other so that the curing reaction occurs in one step, rather than in two. The friction reducing additive is necessary and enough for continuous operation of the pultrusion machine. The amount of aluminum hydroxide may vary according to customer requirements. In this case, was took the middle option. Table 3 presents mass ratio of resin components.

Table 3. Resin mass ratio composition.

| Name	I	II	III	IV
Atlac 430	0.971	0.741	0.934	0.720
Trigonox C	0.015	0.011	0.014	0.011
Perkadox 16	0.005	0.004	0.005	0.004
BYK-A555	0.003	0.003	0.003	0.003
BYK 996	0.006	0.005	0.006	0.005
Zink Stearate	-	-	0.037	0.029
Al(OH)3	-	0.236	-	0.230

Immediately after the resin was prepared, the sealed and labeled containers were transported to the DSC measurement laboratory. Transportation took 1.5 hours and took place under normal conditions at a temperature of 20 degrees. The total measurement time of all samples was more than 6 hours, so to prevent polymerization, the resins were frozen at the measurement in the laboratory of arrival. To do this, they were placed in a freezer with a temperature of -40 degrees.

2.3. DSC measurements

DSC measurements were performed in the laboratory of the CISIS FMT research center at Moscow state University. The author made the measurements independently.

In order to perform DSC measurements of the resin, it is necessary to first prepare samples. The aluminum pans were taken out of the box with clean tweezers to avoid leaving skin and sweat particles on the sample and placed on a high-precision laboratory scale. Next, a sample of resin for scanning was placed in the pan. A wooden toothpick was used to dispense the amount of resin in the pans. The toothpick was dipped in resin, and then the remaining resin on the toothpick was evenly distributed over the bottom of the pans. After that, the pans were weighed, and the resin mass was calculated. If the resin mass was not included in the interval from 5 to 10 milligrams, the procedure was repeated. If the mass of resin in the pans was within the required limits, the crucible was sealed with a special press. Figure 16 presents preparing a specimen before DSC analysis.
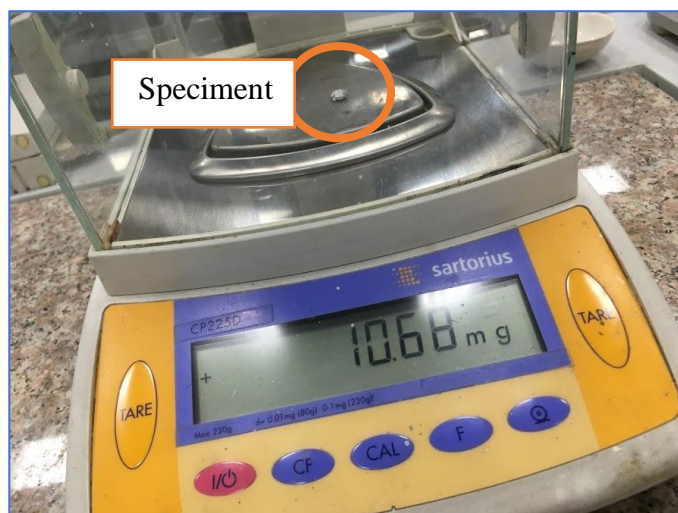
a

b

Figure 16. Speciment preparation before measurements a, speciment on the scales (a), prepaired pressed specimet (b).

Then the prepared specimen is installed in the cell of the DSC. Opening and closing the cell is also performed with tweezers, so as not to leave skin and fat particles on the heated surfaces of the device. After closing the lid, the control program starts (Fig. 17). It selects the desired temperature mode and enters information about the material under study.
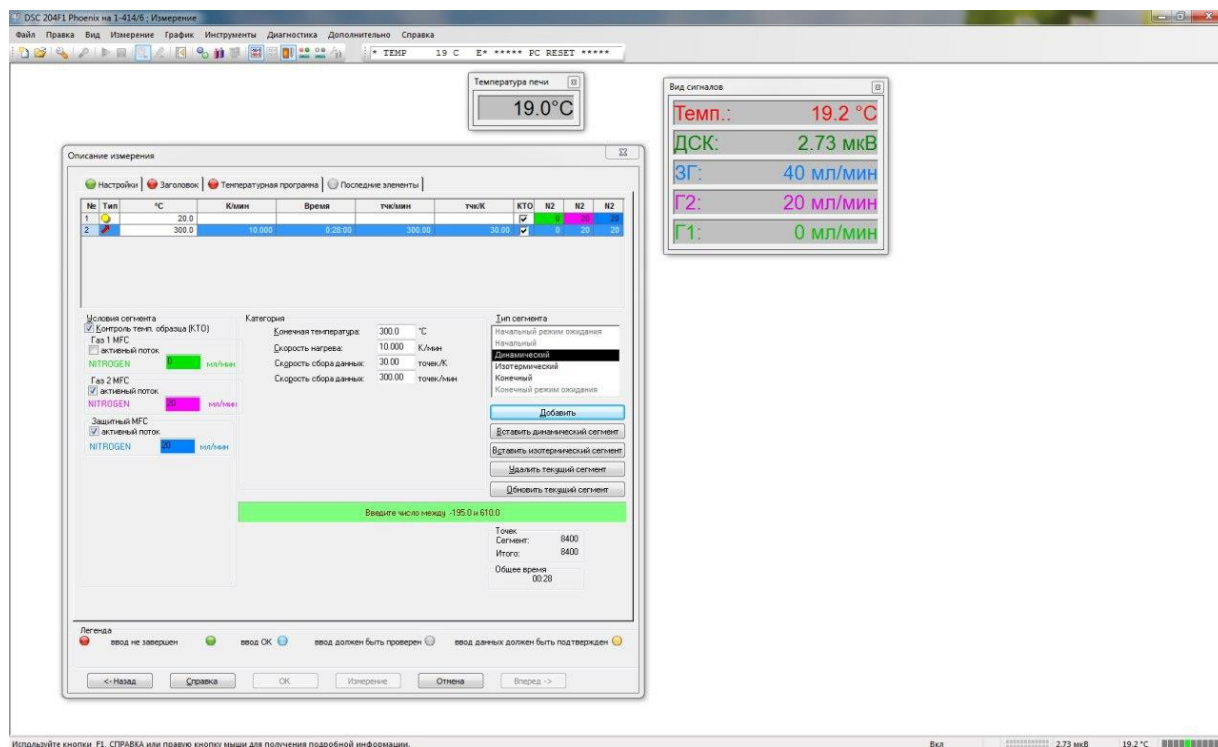

Figure 17. Netzsch Polyma control software screenshot.

After the measurements were made, the measurement data was saved on the computer, and the measured sample was thrown into the shared sample basket. All performed actions are recorded in the laboratory log.

2.4. DSC data processing

The processing was performed in the Netzsch Proteus Thermal Analysis program (Fig. 18). All DSC scans were analysed using this software. For each scan, the start, peak, and end points of polymerization were found. Temperatures for these points were also found, as well as the width of the polymerization peak.

To perform the analysis, a file with measurements was loaded into the program, and files with DSC signal correction made when scanning standards were loaded. After correcting the signal, key points were found sequentially for each measurement.
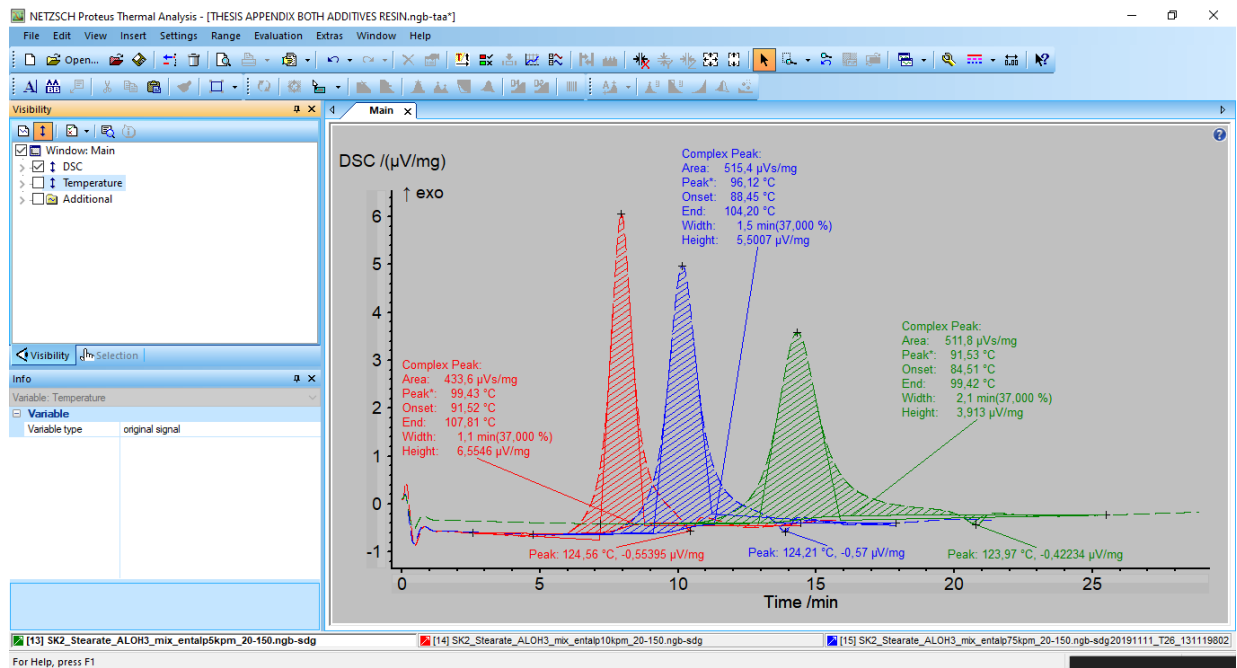
Figure 18. Netzsch Proteus Thermal Analysys software screenshot.

The Netzsch Thermal Kinetic v3.1 program was used to calculate the kinetic equations (Fig 19). It also loaded files with DSC measurements of 3 measurements for each resin. A baseline was built for each dimension. After that, all available linear equations were constructed.

Figure 19. Netzsch Thermal Kinetics software screenshot.

The statistical analysis tool built into the used program allowed us to compare the quality of the calculated models and compare their error.

3. Results

3.1. DSC measurements

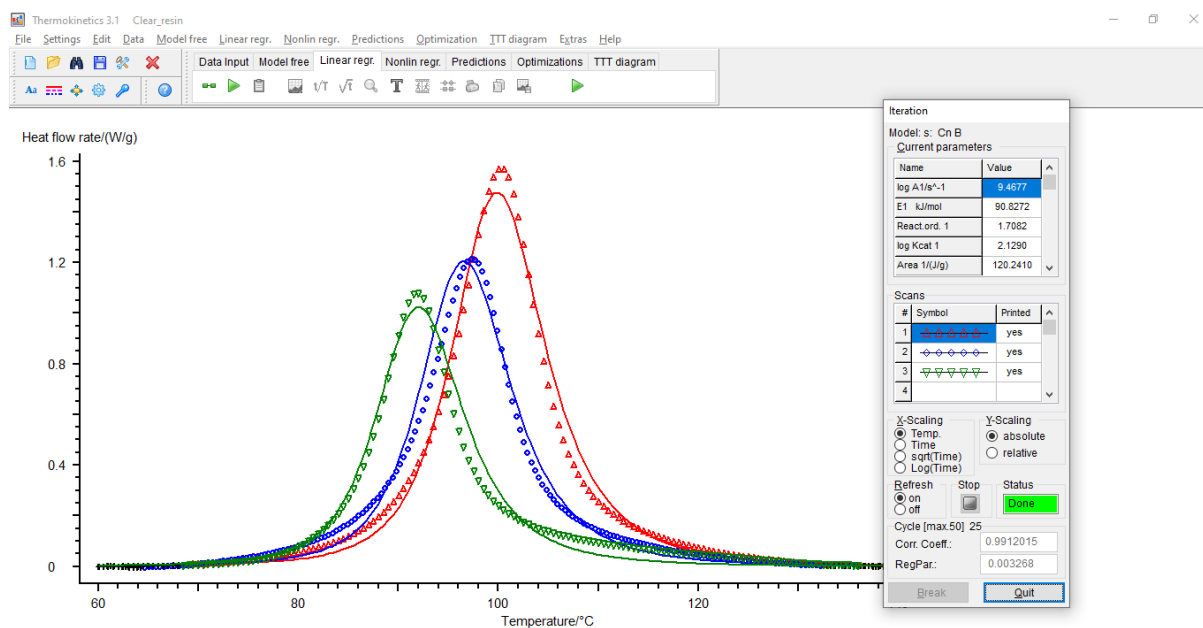A Netzsch Polyma 204 differential scanning calorimeter was used to obtain data on resin polymerization (Fig. 20). The measurements were made according to the international standard[61]. Measurements were taken in the range from 50 to 200 degrees. This temperature regime allowed the use of aluminum pans with a lid. The purge inert gas is Nitrogen. Each container of resin was scanned 3 times at heating rates of 5, 7.5 and 10 Kelvins per minute. Totally 12 specimens were made.

Figure 20. Netzsch Polyma 214 DSC and Dewar's vessel with liquid nitrogen.

A total of 12 measurements were made at speeds of 5. 7.5 and 10 Kelvins per minute. Key points were found for them in accordance with the methodology discussed in paragraph 1.2. the key points Found for each measurement are shown in table 4. Complete measurement results are presented in Appendix 1.

Table 4. Obtained specimens data.

Speciment	Resin	Mass [mg]	Temperature ramp [Kpm]	Peak area [J/g]	Peak [C]	Onset [C]	End [C]	Width [min]	Height [mW/mg]	Base part in mix
1	I	7.44	5	149.7	93.06	85.3	99.63	2.1	1.155	1.00
2	I	8.41	7.5	163.1	97.1	89.22	104.18	1.4	1.79	1.00
3	I	9.99	10	166.7	99.93	92.06	107.81	1.1	2.29	1.00
4	II	7.74	5	130.8	91.8	84.64	98.37	2	1.031	0.77
5	II	9.42	7.5	102.4	97.43	88.61	104.71	1.5	1.14	0.77
6	II	9.78	10	108.9	100.3	91.42	108.13	1.1	1.528	0.77
7	III	7.67	5	210	91.07	84.21	98.89	2.1	1.543	0.96
8	III	7.82	7.5	228.5	95.45	87.52	104.12	1.6	2.24	0.96
9	III	7.84	10	207.4	98.83	90.31	107.85	1.3	2.62	0.96
10	IV	7.63	5	155.5	91.53	84.51	99.42	2.1	1.163	0.75
11	IV	7.31	7.5	159.1	96.12	88.45	104.2	1.5	1.639	0.75
12	IV	8.24	10	142.7	99.43	91.52	107.81	1.1	1.968	0.75

3.2. Additives effects

To study the effect of zinc stearate on the resin polymerization kinetics, the DSC signal for resin 1 and 3 was compared. the scanning Results are shown in figure 21. It presence three measurements for both resins.
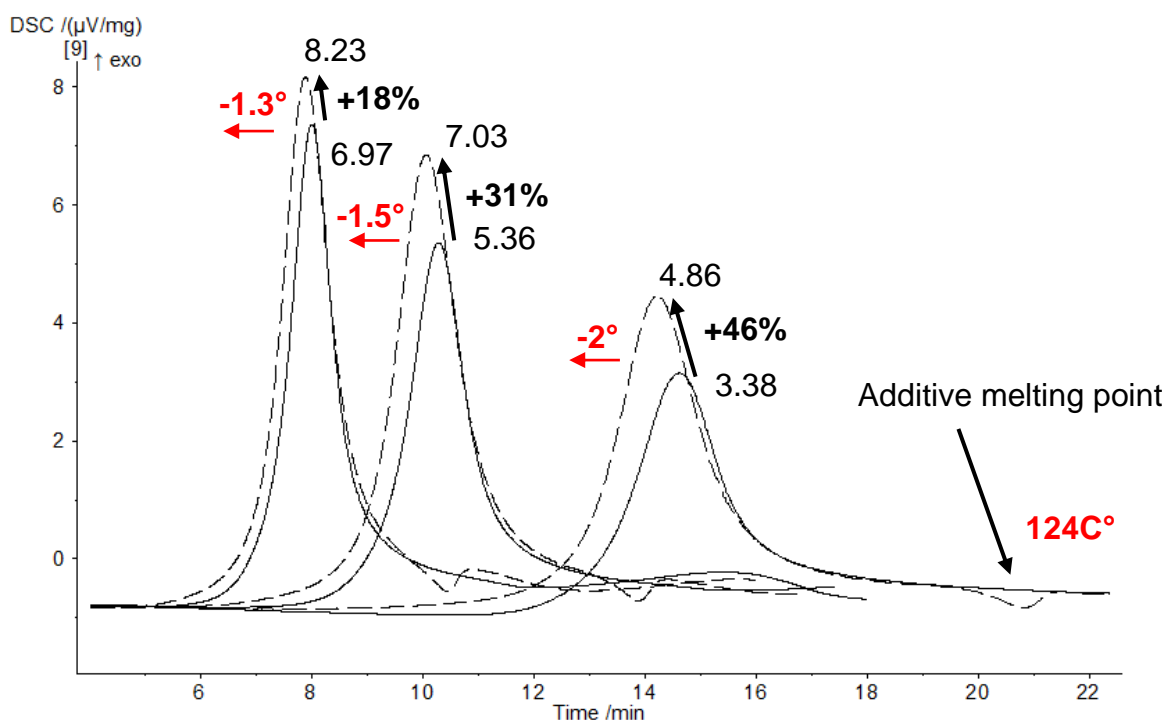

Figure 21. Zink stearate effect.

Figure 21 also presents the peak of melting of zinc stearate appears. In addition, an increase in energy release during polymerization was observed.

Measurements have shown that zinc stearate shifting peaks, as well as increasing their height. It is also seen that the influence of zinc stearate on the height of peaks decreases with an increase in the heating rate from 18% at a heating rate of 10 K/min. Up to 46% at a heating speed of 5kpm. This effect can be explained by the lubricating properties of zinc stearate. The long oligomers of resin and hardener moved faster and reacted faster. The charts also show the peak melting of the zinc stearate additive. To study the effect of aluminum hydroxide, the DSC signals for mixtures 1 and 2 were compared. The results of scanning are presented in figure 22.
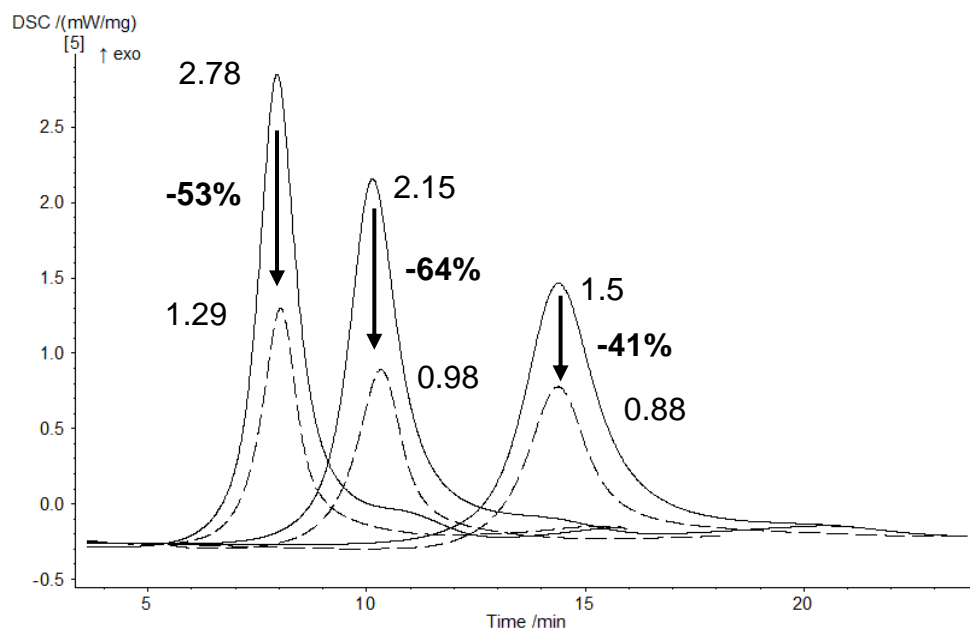
Figure 22. Aluminum hydroxide effect.

To analyse the effect of additives, we will compare the area of graphs-the exhausted energy for all mixtures. Analysis of the data showed that key temperatures independent of the presence of additives in the resin.
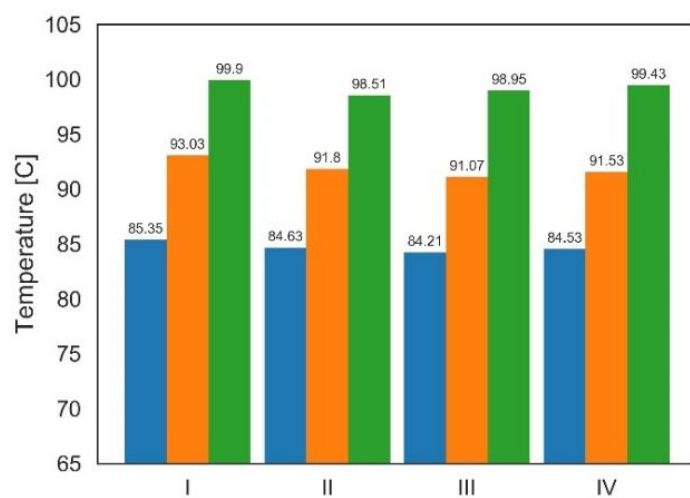

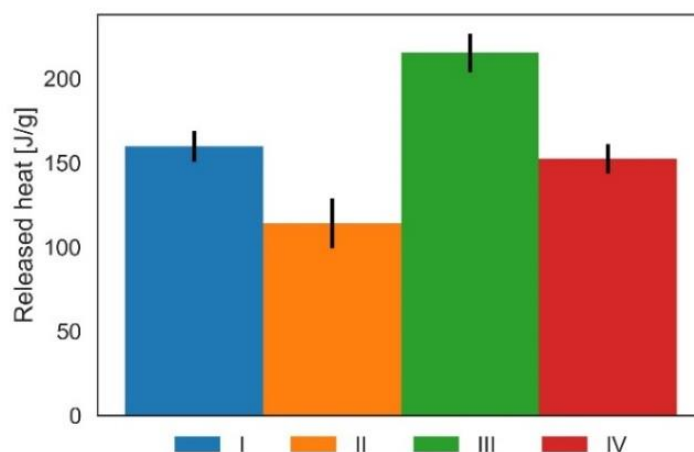Figure 23. Obtained onset, peak, and end points for 5 K/min.

Figure 24. Obtained average released heat(b).

At the same time, additives have a significant effect on released heat amounts. Both additives have an opposite influence on the released heat. The combination of Zink-Stearate and Aluminum hydroxide in the mixture then lead to a final heat of the order as in absence of additives.

The effect of aluminum hydroxide can be explained with a reduced mass ratio of Atlac 430 in the mixture and although the amount of heat released decreased more than the mass of the resin.

The addition of zinc stearate increased the peak area of enthalpy. This shows that the widely used zinc stearate additive is not inert and can have a chemical effect on some resins. The unmatched chemical effect of zinc stearate on the amount of energy released requires further study.

3.3. Resin cure simulation

To describe the kinetics of resin with and without additives the Netzsch thermal kinetics v 3.1 software was used. DSC data was strip from 60 degrees to 145 degrees. Baseline for every measurement was – tangential area proportional. Eighteen kinetics models have been tested, including models described in theoretical chapter. For the described resin, the reaction of n-th order with the autocatalysis model showed the best result for every resin. Table 5 presence a comparison of errors in the calculated models when modeling resin with additives of zinc stearate and aluminum hydroxide.

For clarity of the error, graphs were constructed for the best model - Reaction of Nth order with autocatalysis and the model that showed the worst result - Prout-Tompkins equation. Figure 25 presence correspondence between the constructed models and the data obtained from the differential scanning calorimeter.

Table 5. Calculated kinetic models and their error for mixture IV (with both additives).

Name	Formula	MSE	R2 score

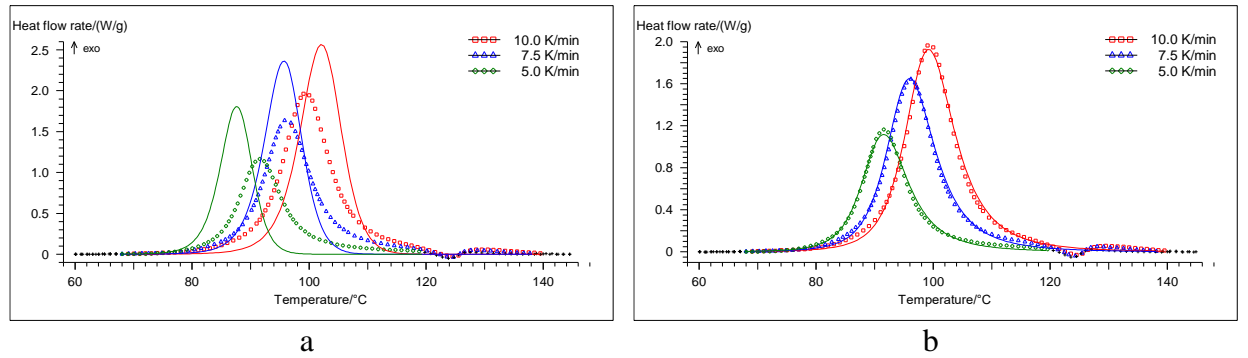|			
Prout-Tompkins equation	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-a)a$	1149.68	0.62
One-dimensional diffusion	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}\dfrac{0.5}{1-a}$	806.16	0.79
Reaction of Nth order	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n$	264.51	0.93
N – dimensional nucleation	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}\alpha(-\ln(1-\alpha)^{n-1})$	151.76	0.96
Expanded Prout-Tompkins equation	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n\alpha^m$	22.53	0.994
Reaction of Nth order with autocatalysis	$\dfrac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n(1+K_{cat}*\alpha)$	10.57	0.998

Figure 25. Resin with both additives DSC signal simulated with Prout-Tompkins equation (a), reaction of n-th order with autpcatalysis(b). Dots – experimental data, lines – simulation.

As can be seen from the results obtained, the autocatalysis reaction model, much better describes the polymerization process of vinyl ether pultrusion resin due to additional parameters. However, it completely ignores the melting of the additive-zinc stearate. Table 6 presents the found kinetic constants for reaction of n-th order with the autocatalysis model and model error for each resin.

Table 6. Obtained kinetic constants for each resin.

	Average H_{tolal}[J/g]	log (A)	Ea [kJ/mol]	n	log (Kcat)	R^2[79]
I	159.83	12.09	108.49	1.71	2.04	0.997
II	114.03	9.48	90.82	1.70	2.13	0.994
III	215.3	8.75	87.92	2.09	2.54	0.992
IV	152,43	9.56	92.94	1.82	2.41	0.991

Using the obtained constants, we simulate the DSC signal and compare it with the received one. This representation allows to estimate the quality of the built model visually. Figures 26 presents experimental and simulated DSC signals for I & IV mixtures.
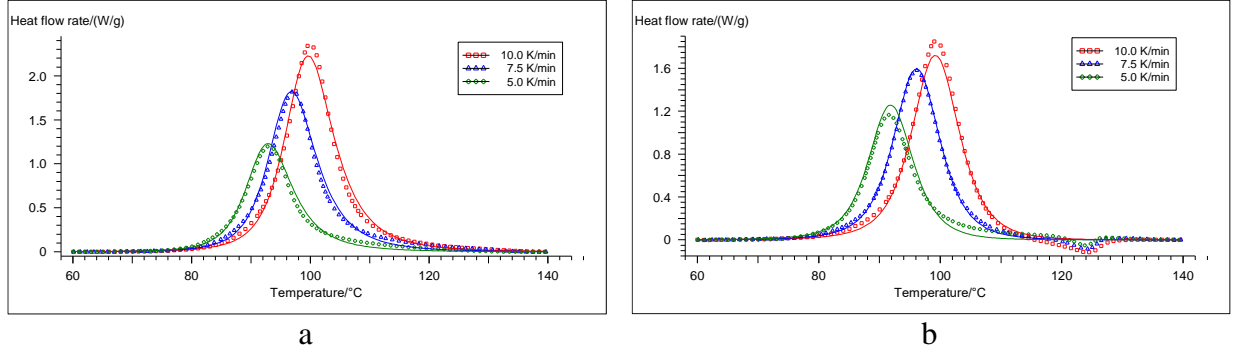
Figure 26. Polymerization enthalpy and mathematical simulation with Nth order reaction with autocatalysis for resin I (a) and IV (b) . Dots – experimental data, lines – simulation.

A downward peak near 125 °C is the melting of the additive – Zinc-stearate. The obtained kinetics clearly showed that additives influence the resin polymerization enthalpy. Due to the superposition of the melting of zinc stearate at the end of the peak polymerization, a slight error in the accuracy of the model arises: R^2 in table 4. This shows that additives can affect the model error.

3.4. Kinetic model refining

As shown above, the presence of additives increases the model error. In this subchapter, we propose an approach allowing a researcher to account for the effect of zinc stearate on the polymerization kinetics of pultrusion resins. In order to reduce the error when describing the resin polymerization process, two separate models were built: the model describing the polymerization of resin with zinc stearate, and the model describing the melting of the additive. The combination of two models would be the mathematical model of a DSC signal obtained for the resin with the additive[87].

$$\frac{d\alpha}{dt} = \frac{d\beta}{dt} + \frac{d\gamma}{dt}$$
(14)

Where: $\frac{d\alpha}{dt}$ is resin mixture curing, $\frac{d\beta}{dt}$ is vinyl ester curing, $\frac{d\gamma}{dt}$ is Zink stearate melting. The separation of the DSC signal was carried out in a following way: near the beginning and end of the melting peak of the additive, points were found that were described with tangent to two points. So, the model for the resin polymerization model was a straight line instead of the melting peak of zinc stearate. The model describing the melting of the additive was calculated based on the difference between the tangent and the downward peak. Thus, the tangent is the base line for the DSC signal of the additive melting. Figure 27 shows the DSC signal with a truncated peak corresponding to the melting of zinc stearate.
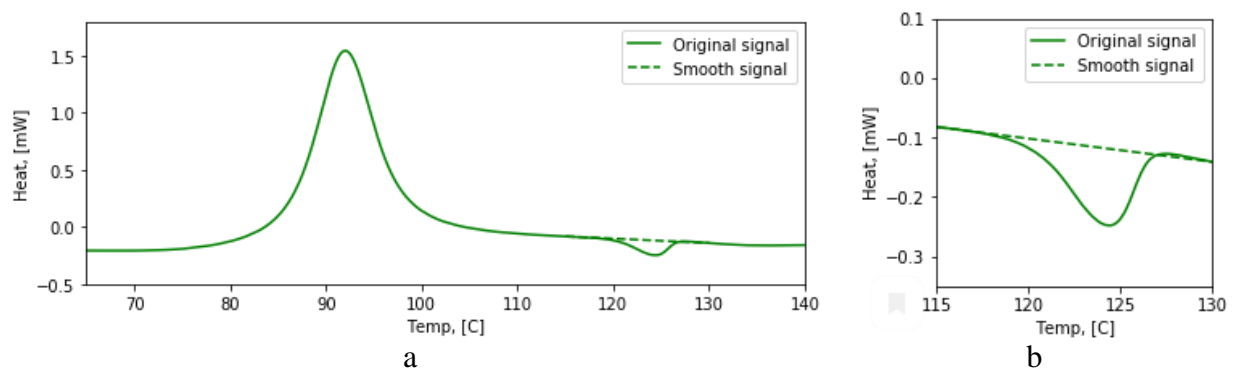
Figure 27. Separation of resin polymerization and additive melting enthalpy (a) and zoomed in (b).

Table 7 presents the obtained model constants describing the original and modified polymerization kinetics vectors for the autocatalysis model of degree N. The calculations were carried out in the kinetics analysis software - Netzsch ThermoKinetics 3.1.

Table 7. Calculated constants for a Nth order reaction with autocatalysis equation.

	H_{total} [J g^{-1}]	log (A)	E_a [kJ mol^{-1}]	n	log (Kcat)
Original data	188.72	9.3375	93.2835	1.914	2.734
Modified data	206.04	9.5294	92.5214	1.7	2.407

The least error in modelling the melting peak of zinc stearate in pultrusion resin was obtained using Avrami-Erofeev's model

$$\frac{d\gamma}{dt} = Ae^{-\frac{Ea}{RT}}(1-\gamma)(-\ln(1-\gamma))^{\frac{1}{n}} \tag{15}$$

The model constants describing this process are given in Table 3. To calculate the kinetic constants, it was also used in the analysis of the kinetics of the software Netzsch ThermoKinetics 3.1.

Table 8. Calculated constants for melting peak with Avrami-Erofeev's model

H_{total} [J g^{-1}]	log (A)	E_a [kJ mol^{-1}]	n
12.73 ± 1.82	118.038	907.0423	0.7951

The resulting graph represents the quality of the data description by the model with found kinetic constants.
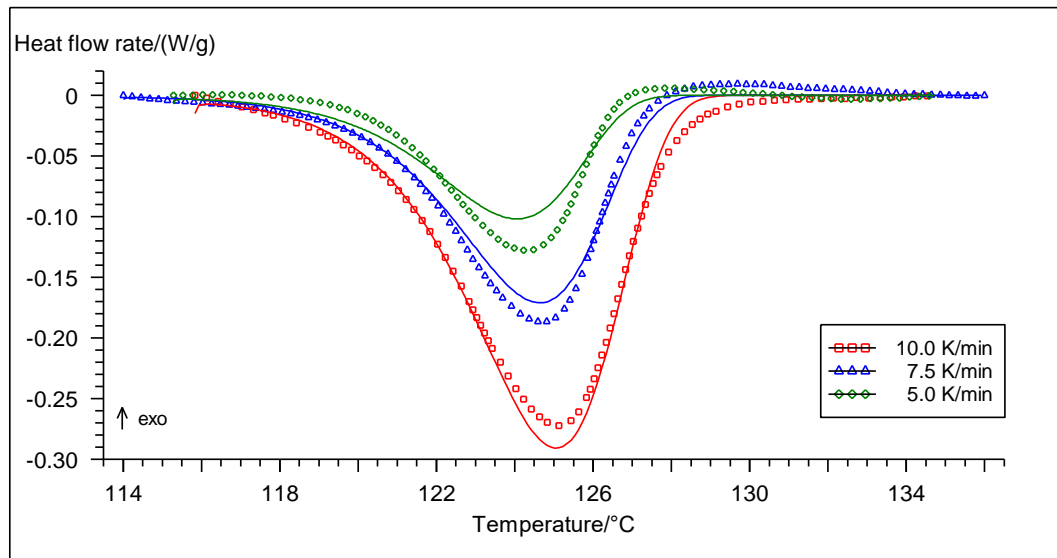
Figure 28. The enthalpy of melting of zinc stearate in the composition of pultruded resin.
Dots – experimental data, lines – simulation.

The graph shows that the model does not perfectly describe the melting of zinc stearate, but the proposed solution will reduce the simulation of the resin with zinc stearate. The table 9 shows a comparison of the quality of the model description for resin with zinc stearate.

Table 9. Statistical model comparison for resin with zinc stearate.

Model	Model equation	Method	R^2[79]	MSE[88]
Reaction of n-th order with autocatalysis	$\frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n(1+K_{cat}*\alpha)$	Classic	0.993	60.51
		Proposed	0.994	54.42
Reaction of 1st order with autocatalysis	$\frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)(1+K_{cat}*\alpha)$	Classic	0.98	180.97
		Proposed	0.985	129.91
Expanded Prout-Tompkins equation	$\frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n\alpha^m$	Classic	0.99	85.44
		Proposed	0.99	84.84

The best result was shown by model «Reaction of n-th order with autocatalysis». The proposed method allowed us to slightly increase the accuracy of the model. In the case of «Reaction of 1 st order with autocatalysis », the average square error was reduced by almost 30%.

3.5. Pultrusion simulations

Simulations were performed based on the obtained kinetic constants. We considered the production process of a thin-walled pultrusion profile. For a thin profile, we can neglect the thermal conductivity and assume that the profile is instantly heated to the temperature of the die. The length of the die is 60 centimeters, the pulling speed is 60 centimeters per minute. The diagram of die is shown in figure 29
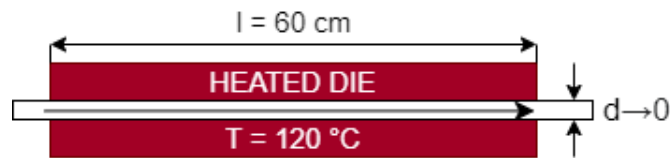
Figure 29.Thin pultrusion die scheme.

Based on the calculated kinetic models, the resin curing process was simulated in the production of a thin-walled pultrusion profile. In the simulation, the profile enters the die heated to 120 degrees. The profile has a small thickness, so the thermal conductivity is neglected. Simulation results are shown in figure 30.
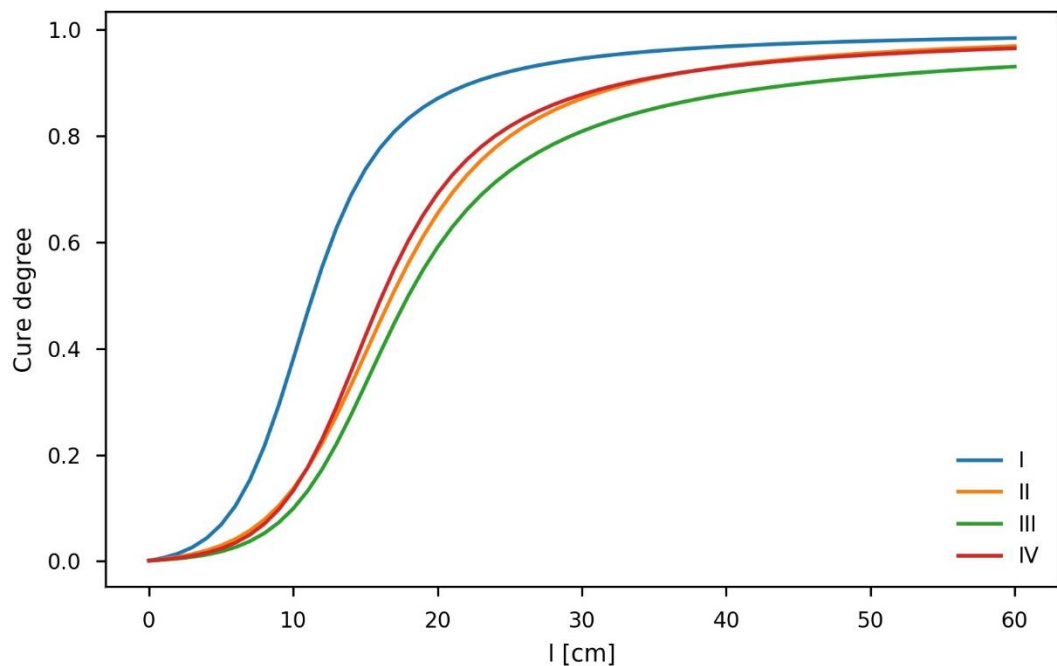

Figure 30. Simulated resin 1 minute isothermal curing at for all mixtures at 120 °C simulated with Nth order reaction with autocatalysis equation.

The graph shows that the fastest cures resin from container I, the slowest of all from container III. The curing of mixtures II and IV is almost the same. The table 5 presents simulated cure degree after minute at 120 degrees.

Table 10.The cure degree of the thin-walled pultrusion profile at the end of the die.

	I	II	III	IV
Cure degree	98.4%	96.9%	93%	96.5%

At first glance, it seems that the difference in the degree of polymerization of different resin compositions is not so large. However, we considered the following problem, which is closer to production.

Determine the maximum extraction speed of the cured composite. We will assume that the cured composite is a composite with a degree of resin polymerization of 95%. For the each mixture, the polymerization process was simulated at the die temperature and the required time for

polymerization was calculated. Graphs of the dependence of the degree of polymerization on the heating time are shown in figure 31.
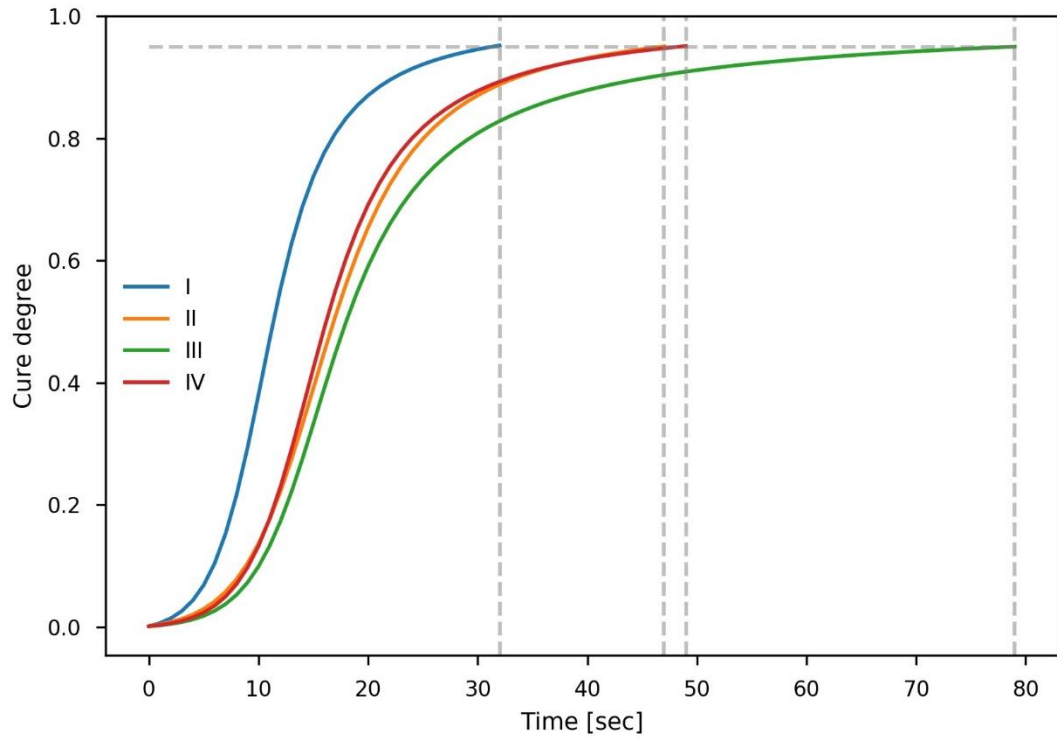

Figure 31. Required time for isothermal curing at for all mixtures at 120 °C simulated with Nth order reaction with autocatalysis equation.

After the simulation, we obtained the required polymerization time. Considering the length of the die, we can calculate the required production speed of the pultrusion profile. The production speed is calculated as the ratio of the length of the die to the polymerization time (14).

$$pulling\ speed\ [\frac{cm}{min}] = \frac{die\ lenth\ [cm]}{curing\ time\ [min]} \tag{16}$$

Table 11. Required time and speed of extraction to obtain a 95% cured composite with different resins.

	I	II	III	IV
Curing time [sec]	31	47	79	49
Pulling speed [cm/min]	116	76	46	73

The maximum difference with the production speed between resins 3 and 1. They differ by 2.5 times. Under the conditions of this problem of modeling the production of a thin-walled pultrusion profile, additives show a significant impact on the maximum productivity of the pultrusion plant.

The results obtained in this subchapter show that additives used in the pultrusion composites production industry could change the kinetic characteristics of the resin used. In the case of vinyl ether Atlac 430 resin, significant differences in the released energy, as well as

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insignificant changes, were detected at the points of offset, peak, and end of the polymerization reaction.

The influence of these parameters additionally entailed an influence on the kinetic model constants. Was calculated resin curing simulation, which showed a significant difference in used mixtures cure rate. This effect means that modelling of resin curing in production must be carried out based on DSC scans of the final resin mixture. It is not possible to optimize production parameters based on cure kinetics of just resin with hardeners.

Simulation of the pultrusion process showed that the performance of the pultrusion plant could differ by 2.5 times, depending on the concentration of process additives.

Next, we considered the impact of model selection on simulation results. To do this, we repeated the previous task, only in this case, we compared the resin polymerization with zinc stearate and aluminum hydroxide, described by different models. We compared the model showing the most significant error – the Prout Tomkins equation, the model with the smallest error – the Nth order reaction autocatalysis equation, and the proposed method with the separation of modeling the peak of resin polymerization and melting of the additive. Results of simulation are presented at figure 32.
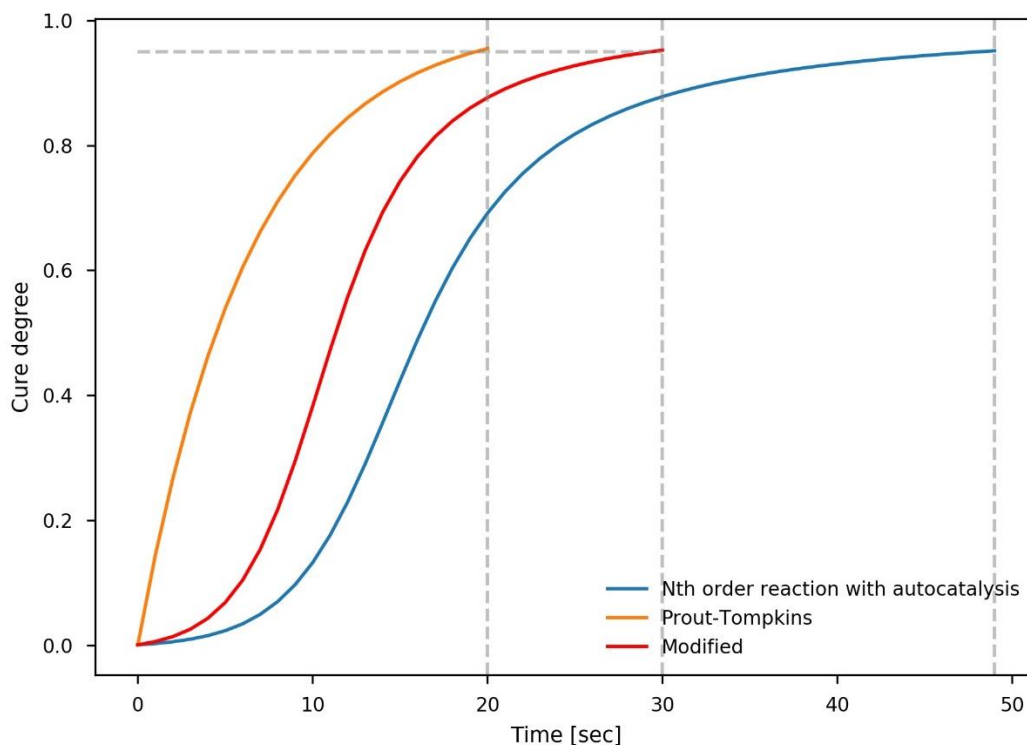

Figure 32. Pultrusion simulation with different models for IV mixture (with Zinc-Stearate and Al(OH)3).

The simplest model – the Prout Tomkins equation shows the highest resin curing rate. The lowest curing rate was shown by the Nth order reaction autocatalysis equation. The result of the model that used peak separation showed an average result. The pultrusion rate was calculated in

the same way as in the previous simulation using the formula (14). The results of model comparison are shown in table 12.

Table 12. Required time and speed of extraction to obtain a 95% cured composite, described by different models

	Prout-Tompkins	Reaction n-th order with autocatalysis	Modified
Curing time [sec]	49	20	30
Pulling speed [cm/min]	73	180	120

       The obtained values show that the choice of the resin polymerization model significantly affects the results of simulation of the pultrusion process. The model with separated peaks of etheric resin polymerization and zinc stearate melting is the most complex and should better describe the behavior of vinyl-etheric pultrusion resin.

4. Discussion

To achieve the goal of refining the simulation of the pultrusion resin cure kinetics, the influence of technological additives on the pultrusion composite production simulation was studied. An experiment was conducted under Atlac 430 pultrusion resin with different additives. Further, the effect of additives on resin cure kinetics was studied. Mathematical models describing the polymerization process of resins with different additives are constructed. Moreover, the simulation of a thin-walled pultrusion profile production is performed.

Simulations showed a significant influence of additives, as well as methods of modeling resin curing on the optimal production parameters, and consequently on the optimal production speed.

The results obtained mean that pultrusion industry should pay more attention to resin curing simulating in order to optimize the production parameters. We recommend separating the resin cur kinetics and the melting kinetics of the friction-reducing additive Zinc stearate. The refinement of resin polymerization description in composite profiles production will have a significant impact on the daily amount of profile produced and will have a positive impact on the economy of the production process.

In this paper, the influence of zinc stearate and aluminum hydroxide additives has been studied. However, a number of technological additives used pultrusion industry is much larger. During this work, we did not study the effect of used additives: deaerator BYK-A555 and wetting BYK-W996. As well as Zinc stearate and aluminum hydroxide, these widely used in pultrusion additives can affect the cure kinetics of pultrusion resins. Furthermore, thus, they could affect the optimization of pultrusion production.

Moreover, the pultrusion industry uses many other technological additives that we have not touched upon in current work. For example, there are additives for protection against biological effects: they prevent the propagation of various fungi and mold. There are also additives that protect the polymer from the destructive effects of ultraviolet light. Besides, several aesthetic additives serve to give the pultrusion composite color.

In addition to studying the effects of various additives, there is an area of new approaches to resin curing description. The topic of using neural networks for modeling resin polymerization is not fully disclosed due to the rapid development of machine learning methods at present. This leaves the ability for future research into the possibility of deep machine learning in the simulation of pultrusion resins. The hypothesis is that the neural network allows us to build more accurate models of the kinetics of resin polymerization. Most literature sources on neural networks use the simplest single-layer neural networks to model the kinetics of curing composite resins. When modeling other chemical processes, the implementation of neural networks has been more

successful, and the implementation of more modern models, such as recurrent neural networks, is also being studied.

In the course of this work, simulations of the production of a thin-walled profile at constant temperature were performed. For further simulations, more complex models should be used, considering more parameters described in the analytical literature review. This will allow simulation of profiles with a more complex cross-section considering their thickness.

The study of the effect of technological additives on the pultrusion profile production and refinement of cure kinetics description methods will significantly increase the productivity of the pultrusion unit and reduce the cost of manufactured products.

5. Conclusions

This paper describes the influence of methods for cure kinetics simulation and the presence of technological additives on the pultruded composites production simulating. The research included measurements of pultrusion vinyl ether with various additives, construction of their kinetic models, and simulating of a thin-walled pultrusion profile production.

During the experimental part of the work, we noticed that the additives zinc stearate and aluminum hydroxide affect the DSC signal. Aluminum hydroxide reduced the height of the signal peaks, which means that the specific amount of heat generated decreased. This effect is explained by the high mass fraction of the additive in the mixture. By adding aluminum hydroxide, we reduced the mass ratio of vinyl ester resin and hardeners. Zinc stearate increased the height of the signal peaks and therefore increased the specific amount of heat generated. Also, it slightly shifted the temperature of the peaks down. The lubricating properties of zinc stearate can explain this effect. The long oligomers of resin and hardener moved faster and reacted with increased heat flow. At the same time, if both additives were present in the resin, they leveled the effect of each other. The released hat amount of the resin with both additives is equaled to the resin without additives at all.

During describing the kinetics of resin polymerization, we saw that the smallest error showed the Nth order reaction with the autocatalytic equation, and the worst solution for modeling a vinyl ester was the Prout-Tomkins equation. The reason is that the Nth order reaction with autocatalysis equation has a higher number of parameters and therefore is better able to describe complex reactions. However, despite a small error, the Nth order reaction with the autocatalytic equation is ignored the zinc stearate melting.

For a better description of the polymerization model of vinyl resin with additives, a method for separating the polymerization genetics and the melting additive genetics was proposed. The proposed method reduced the error. The most significant effect was for the reaction of autocatalysis of the first degree. Its error was reduced by 30 %.

For a detailed study of the additives effect on the pultrusion production simulation results, the problem of simulating the a thin-walled pultrusion profile production was solved. First, the cure degree of resins with different additives was estimated when passing through a heated die. The pure resin obtained the highest cure degree at the exit from the die. The lowest result showed resin with zinc stearate. After the required extraction speed to produce a rejected pultrusion profile among all resins was calculated. The resin with zinc stearate showed almost three times less speed than the resin without additives.

Next, the pultrusion production for resin with additives: zinc stearate and aluminum hydroxide simulation was carried out with various mathematical models: Prout-Tomkins equation, the Nth order reaction with autocatalysis model, and proposed solutions with separation of

polymerization kinetics and additive melting genetics. Observed models showed significant discrepancies. Significant differences in the simulation results depending on the presence of additives, and the selected kinetic model shows that the area of studying the kinetics of pultrusion resin requires attention, and simulation results must be confirmed experimentally.

For the pultrusion industry, these results mean that more attention should be paid to the definition and modeling of resin cure kinetics because this leads to significant changes in the simulation and optimization of the release of the pultrusion profile. It is also necessary to simulate the polymerization kinetics of pultrusion resin as the sum of the resin polymerization kinetics and the melting kinetics of the lubricant additive. A deeper study of the kinetics of polymerization will help to optimize better the process of producing pultrusion composites and increase the daily produced amount by tens of percent.

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APPENDIX A – DSC measurements data
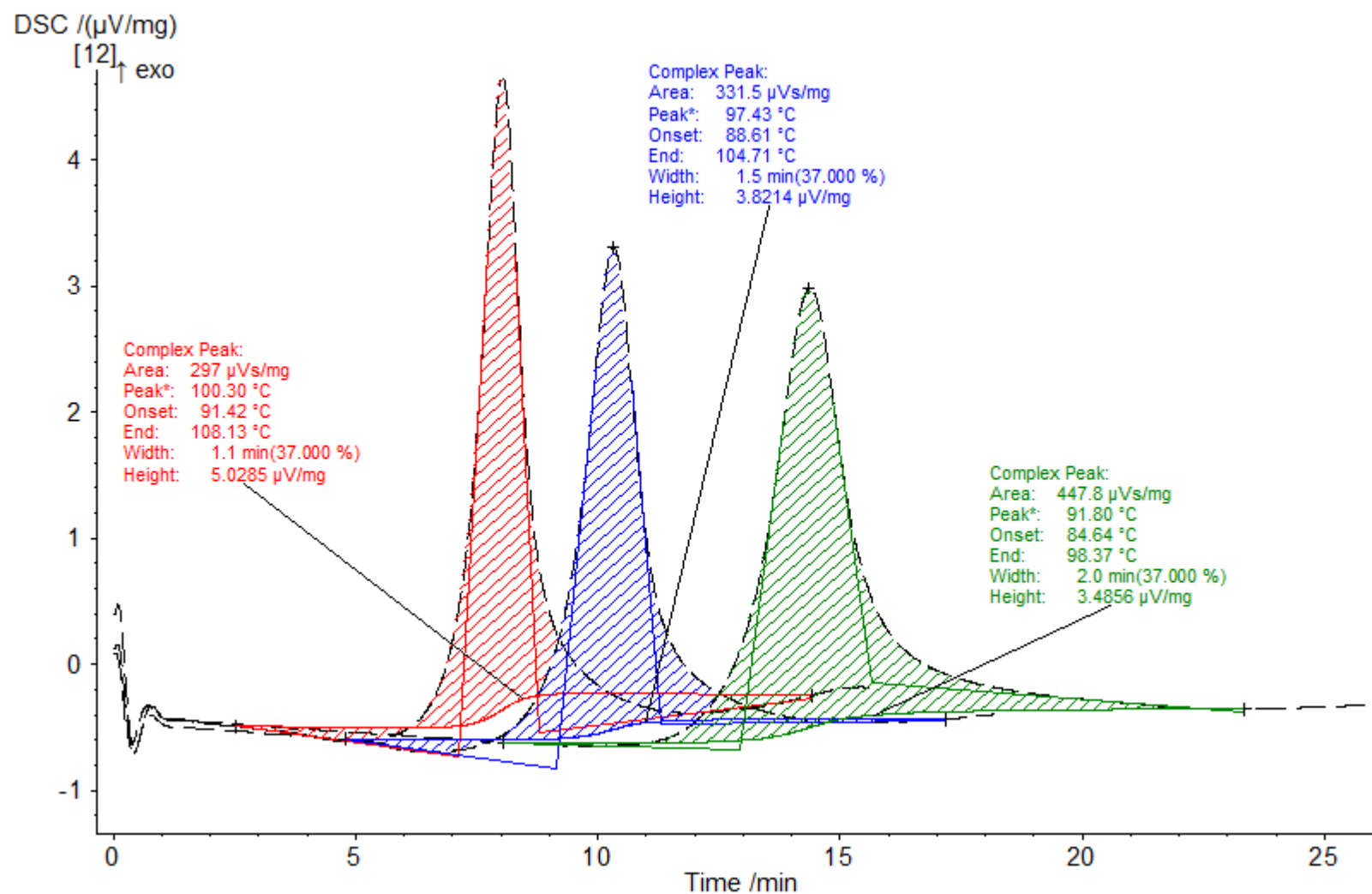

Figure 1. Obtained DSC signal for pure resin (I).
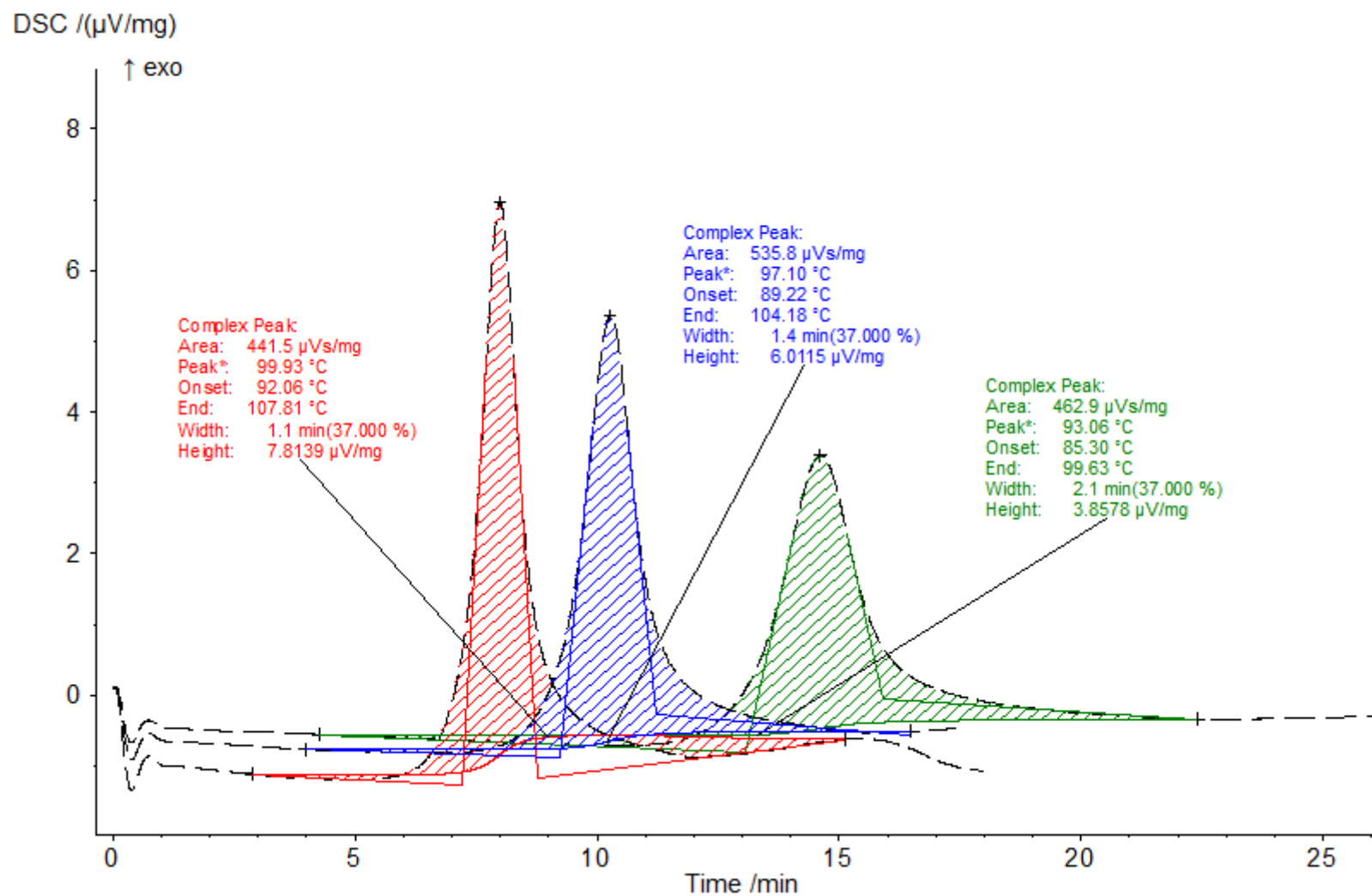
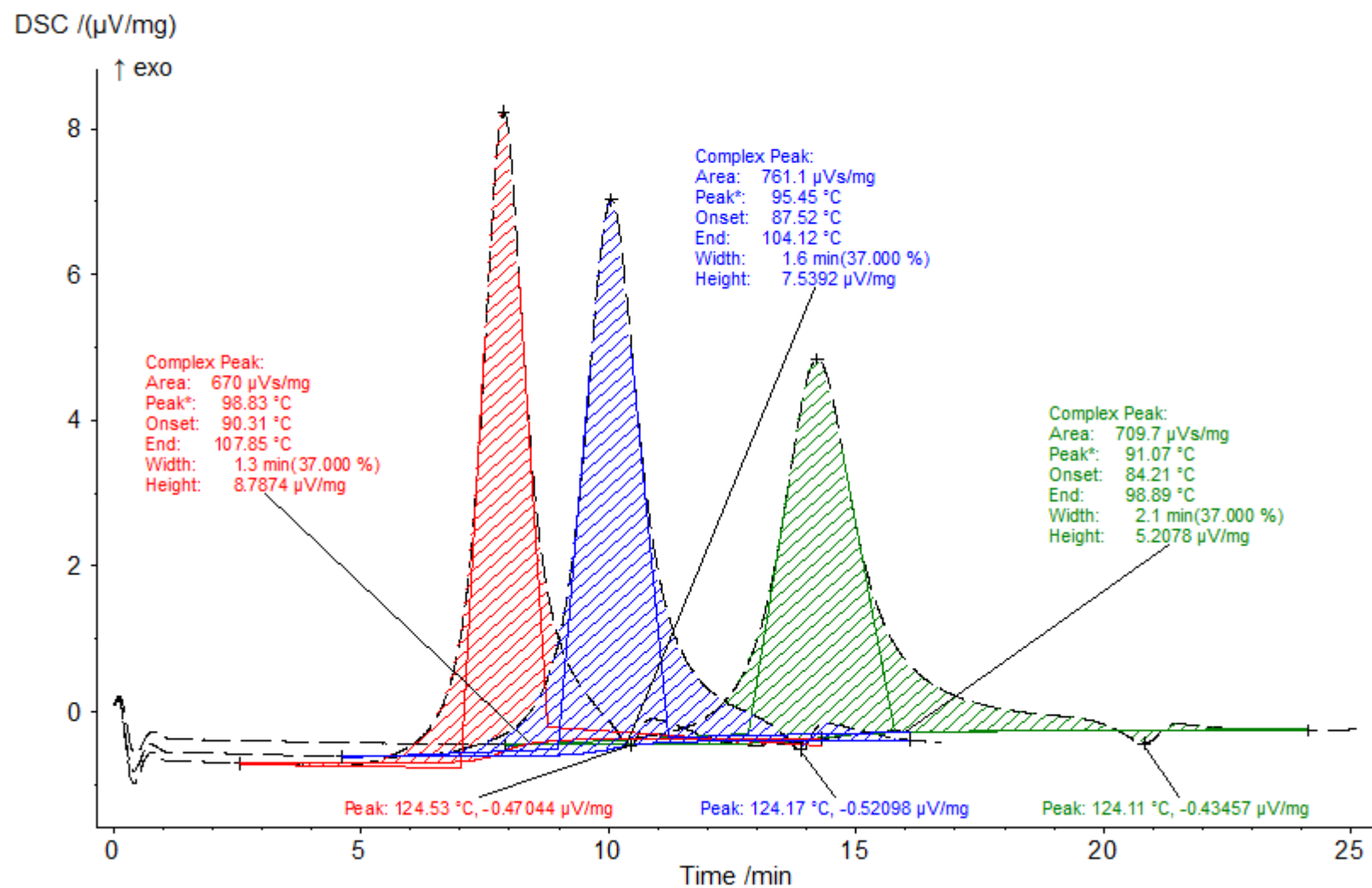Figure 2. Obtained DSC signal for resin with Al(OH)3 (II).

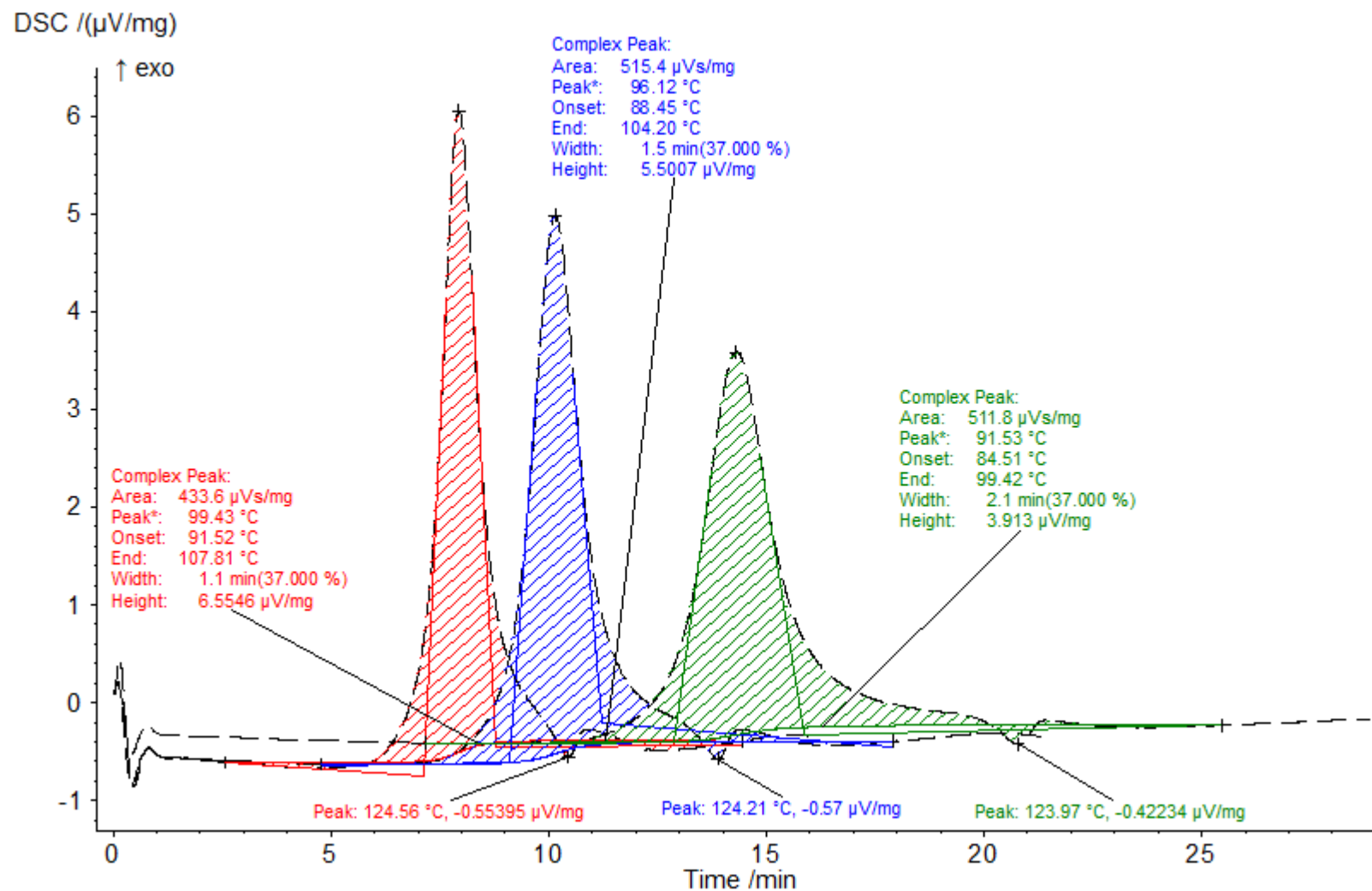Figure 3. Obtained DSC signal for resin with Zinc-Stearate (III).

Figure 4. Obtained DSC signal for resin with Al(OH)3 and Zinc-Stearate (IV).