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CONTENTS

PHYSICS

M.B. Albatyrova

Energy evolution equation in a nonlinear spin system: derivation and numerical modeling.....11

E.A. Dmitriyeva, A.E. Kemelbekova, A.K. Shongalova, O.A. Shilova

Effect of the precursor concentration on the morphology and photosensitivity of the resulting ZnO thin films.....21

A. Istlyaup, L. Myasnikova, A. Lushchik

Computer simulation of the electrical properties of a carbon sheet with alkali metal iodide crystals.....33

A. Kenesbayeva, Ye.I. Kuldeev, E.O. Shalenov, T.B. Nurpeissova

Determination of the gravitational constant.....49

Sh.T. Nurmakhmetova, N.L. Vaidman, S.A. Khokhlov, A.T. Agishev, A.A. Khokhlov

The emission-line dusty object IRAS 07080+0605: evidence for binarity.....60

E.Otunchi, A.A. Migunova, A.Umirzakov, N.Tokmoldin

Effect of the composition of the film-forming system on the properties of SnO₂ films obtained by spray pyrolysis.....71

U.A. Ualikhanova, A.N. Abdipatta, O.V. Razina, A.M. Syzdykova, G.S. Altayeva

Bulk viscosity in f(T) gravity and its impact on cosmological evolution.....83

A.Zh. Umirbayeva, L. Aktay, L.N. Kondratyeva, I.M. Izmailova, A. Shomshekova

Methodology for the reduction of archival slit spectra of planetary nebulae.....99

N. Eghtesadi, S.S. Uzakbaeva, Z.K. Aimaganbetova, N.N. Zhanturina, A.Z. Bekeshev

Prediction of the kinetic properties of low-density polyethylene.....115

D. Yurin, D. Kuvatova, A. Glushenko, Ch. Omarov, M. Makukov

Analysis of the limits of direct n-body simulation using Nvidia RTX4090 GPU cards.....131

CHEMISTRY

- A.S. Beisenova, A.A. Zhanybekova, M.M. Duysebaeva, G.E. Berganaeva**
Study of the chemical composition of *Centaurea diffusa* Lam. growing in the territory of Almaty region.....146
- N.N. Berikbol, Zh.S. Kassymova, L.K. Orazzhanova, A.N. Klivenko, N.N. Nurgaliyev**
Synthesis of interpolyelectrolyte complexes from fluorescently labeled biopolymers.....161
- O.A.Yessimova, S.Sh. Kumargaliyeva, B.K. Musabekov, A.K. Konysbek**
Colloidal - chemical properties of alhagi and tansy (*tanacetum*) hydrolates.....182
- R.N. Zhanaliyeva, B. Imangaliyeva, B. Torsykbaeva, R. Kozykeyeva**
Catalytic hydrogenation of carbonyl-containing compounds: mechanism, catalysts and application.....193
- M.A. Zhumash, K. Tilegen, Y.A. Boleubayev, S.S. Itkulova**
Dry reforming of methane over the high active Co-Fe-Ir-containing alumina supported catalyst.....207
- M. Ibrayeva, N. Sagdollina, Zh. Mukazhanova, Sh. Sanyazova, M.Ozturk**
Optimization of flavonoid extraction conditions from a plant of the genus *Symphotrichum novi-belgii*.....218
- M.K. Kurmanaliev, Zh.E. Shaikhova, S.O. Abilkasova**
Supramolecular polymeric receptors for binding alkali metal ions.....228
- Y.A. Mussatay, M.I. Tulepov**
Carbon filters from rice husk for air purification in confined spaces.....238
- A.Zh. Mutushev, A.B. Seisenova, O.S. Kapizov, A.M. Nuraly, D.K. Mukhanov**
Integrated process for the synthesis of carbon-silicon nanocomposites from biowaste and metallurgical sludge.....258
- A.S. Sass, I.I. Torlopov, K.S. Rakhmetova, D.A. Zhumadullaev, M. Zhurinov**
Influence of metal surface mechanical preparation on the properties of phosphate coatings.....274

МАЗМҰНЫ

ФИЗИКА

М.Б. АльбатыроваСызықтық емес спиндік жүйедегі энергия эволюциясының теңдеуі:
шығарылуы және сандық модельдеу.....11**Е.А. Дмитриева, А.Е. Кемелбекова, А.Қ. Шонғалова, О.А. Шилова**Прекурсор концентрациясының алынған жұқа ZnO жабындарының
құрылымы мен фотосезімталдығына әсері.....21**Н. Эхтесади, С.С. Узакбаева, З.К. Аймаганбетова, Н.Н. Жантурина,
А.З. Бекешев**Төмен тығыздықтағы полиэтиленнің кинетикалық қасиеттеріне
болжау жасау.....33**А. Истляуп, Л. Мясникова, А. Лущик**Сілтілі металл иодидтерінің кристалдарымен көміртек қабатының
электрлік қасиеттерін компьютерлік модельдеу.....49**А. Кенесбаева, Е. Кульдеев, Е. Шаленов, Т. Нурпеисова**

Гравитациялық тұрақтыны анықтау.....60

Ш.Т. Нурмахаметова, Н.Л. Вайдман, С.А. Хохлов, А.Т. Агишев, А.А. Хохлов

IRAS 07080+0605 эмиссиялық объекті: екіжұлдыздық жүйенің дәлелі.....71

Е. Отунчи, А.А. Мигунова, А.Г. Умирзаков, Н. ТокмолдинЖабын түзуші жүйе құрамының спрей-пиролиз әдісімен алынған
SnO₂ жабындарының қасиетіне әсері.....83**У.А. Уалиханова, А.Н. Әбдіпатта, О.В. Разина, А.М. Сыздыкова, Г.С. Алтаева**f(T) гравитациясындағы көлемдік тұтқырлық және оның
космологиялық эволюцияға әсері.....99**А.Ж. Умирбаева, Л. Актай, Л.Н. Кондратьева, И.М. Измайлова,
С.А. Шомшекова**Планетарлық тұмандықтардың архивтік саңылаулы спектрлерін
өңдеу әдістемесі.....115**Д. Юрин, Д. Куватова, А. Глущенко, Ч. Омаров, М. Макуков**N-бөлшекті тікелей үлгілеудің шектерін Nvidia RTX 4090
GPU-карталарын пайдаланып талдау.....131

ХИМИЯ

- А.С. Бейсенова, А.А. Жаныбекова, Г.Е. Берганаева, М.А. Дюсебаева**
Алматы облысының аумағында өсетін шашыңқы гүлкекіре *Centaurea diffusa Lam.* өсімдігінің химиялық құрамын зерттеу.....146
- Н.Н. Берікбол, Ж.С. Касымова, Л.К. Оразжанова, А.Н. Кливенко, Н.Н. Нурғалиев**
Флуоресцентті таңбаланған биополимерлерден интерполиэлектрлиттік комплексті синтездеу.....161
- О.А. Есимова, С.Ш. Құмарғалиева, К.Б. Мусабеков, А.Қ. Қонысбек**
Жантақ және түймешетен гидрولاتтарының коллоидтық-химиялық қасиеттері.....182
- Р.Н. Жаналиева, Б. Иманғалиева, Б.Б. Торсыкбаева, Р. Козыкеева, Р.Э. Ходжаназаров**
Құрамында карбонил бар қосылыстардың каталирикалық гидрогенизациясы: механизмі, катализаторлары және қолданылуы.....193
- М.А. Жұмаш, К.Т. Тілеген, Е.А. Болеубаев, Ш.С. Итқұлова**
Алюминий тотығына қондырылған жоғары белсенді Co-Fe-Ir құрайтын катализатордағы метанның құрғақ риформингі.....207
- М. Ибраева, Н. Сағдоллина, Ж. Мукажанова, Ш. Саньязова, М. Ozturk**
Symphyotrichum novi-belgii тұқымдас өсімдіктен флавоноидтарды алу жағдайларын оңтайландыру.....218
- М.Қ. Құрманалиев, Ж.Е. Шаихова, С.О. Әбілқасова**
Сілтілік металл иондарын байланыстыруға арналған супрамолекулалық полимерлік рецепторлар.....228
- Е.А. Мұсатай, М.И. Тулепов**
Шағын кеңістіктегі ауаны тазартуға арналған күріш қауызы негізіндегі көміртек құрамды сүзгілер.....238
- А.Ж. Мутушев, А.Б. Сейсенова, Ө.С. Капизов, Ә.М. Нұралы, Д.К. Муханов**
Биоқалдықтар мен металлургиялық шламнан көміртек-кремний нанокөміртектерін синтездеудің интеграцияланған әдісі.....258
- А.С. Сасс, И.И. Торлопов, К.С. Рахметова, Д.А. Жумадуллаев, М. Журинов**
Металдар бетін механикалық дайындаудың фосфатты жабындар қасиеттеріне әсері.....274

СОДЕРЖАНИЕ

ФИЗИКА

М.Б. АльбатыроваУравнение эволюции энергии в нелинейной спиновой системе:
вывод и численное моделирование.....11**Е.А. Дмитриева, А.Е. Кемелбекова, А.Қ. Шонғалова, О.А. Шилова**Влияние концентрации прекурсора на морфологию и фоточувствительность
получаемых тонких пленок ZnO.....21**А. Истляуп, Л. Мясникова, А. Лущик**Компьютерное моделирование электрических свойств углеродного листа
с кристаллами йодидов щелочных металлов.....33**А. Кенесбаева, Е. Кульдеев, Е. Шаленов, Т. Нурпеисова**

Определение гравитационной постоянной.....49

Ш.Т. Нурмахаметова, Н.Л. Вайдман, С.А. Хохлов, А.Т. Агишев, А.А. ХохловЭмиссионный пылевой объект IRAS 07080+0605: доказательство двойной
природы.....60**Е. Отунчи, А.А. Мигунова, А.Г. Умирзаков, Н. Токмолдин**Влияние состава пленкообразующей системы на свойства пленок
SnO₂, полученных методом спрей-пиролиза.....71**У.А. Уалиханова, А.Н. Эбдіпатта, О.В. Разина, А.М. Сыздыкова, Г.С. Алтаева**Объемная вязкость в f(T) гравитации и ее влияние
на космологическую эволюцию.....83**А.Ж. Умирбаева, Л. Актай, Л.Н. Кондратьева, И.М. Измайлова,
С.А. Шомшекова**

Методика обработки архивных щелевых спектров планетарных туманностей...99

**Н. Эхтесади, С.С. Узакбаева, З.К. Аймаганбетова, Н.Н. Жантурина,
А.З. Бекешев**

Прогнозирование кинетических свойств полиэтилена низкой плотности.....115

Д. Юрин, Д. Куватова, А. Глущенко, Ч. Омаров, М. МакуковАнализ пределов прямого моделирования n-тел с использованием
GPU-карт Nvidia RTX4090.....131

ХИМИЯ

- А.С. Бейсенова, А.А. Жаныбекова, М.А. Дюсебаева, Г.Е. Берганаева**
Исследование химического состава василек раскидистый *Centaurea diffusa* Lam., растущий на территории Алматинской области.....146
- Н.Н. Берікбол, Ж.С. Касымова, Л.К. Оразжанова, А.Н. Кливенко, Н.Н. Нурғалиев**
Синтез интерполиэлектrolитных комплексов на основе флуоресцентно-меченых биополимеров.....161
- О.А. Есимова, С.Ш. Кумарғалиева, К.Б. Мусабеков, А.Қ. Қонысбек**
Коллоидно-химические свойства гидратов верблюжьей колючки и пижмы...182
- Р.Н. Жаналиева, Б. Иманғалиева, Б.Б. Торсықбаева, Р. Қозықеева, Р.Э. Ходжаназаров**
Каталитическое гидрирование карбонилсодержащих соединений: механизм, катализаторы и применение.....193
- М.А. Жұмаш, К.Т. Тілеген, Е.А. Болеубаев, Ш.С. Иткулова**
Сухой риформинг метана на высокоактивном Co-Fe-Ir содержащем нанесенном на оксид алюминия катализаторе.....207
- М. Ибраева, Н. Сағдоллина, Ж. Мукажанова, Ш. Саньязова, М. Ozturk**
Оптимизация условий экстракции флавоноидов из растения рода *Symphotrichum novi-belgii*.....218
- М.К. Курманалиев, Ж.Е. Шаихова, С.О. Абилкасова**
Супрамолекулярные полимерные рецепторы для связывания ионов щелочных металлов.....228
- Е.А. Мұсатай, М.И. Тулепов**
Углеродные фильтры из рисовой шелухи для очистки воздуха в стесненных помещениях.....238
- А.Ж. Мутушев, А.Б. Сейсенова, О.С. Капизов, А.М. Нуралы, Д.К. Муханов**
Интегрированная технология получения углеродно-кремниевых нанокомпозитов из биоотходов и металлургических шламов.....258
- А.С. Сасс, И.И. Торлопов, К.С. Рахметова, Д.А. Жумадуллаев, М. Журинов**
Влияние механической подготовки поверхности металла на свойства фосфатных покрытий.....274

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PREDICTION OF THE KINETIC PROPERTIES OF LOW-DENSITY POLYETHYLENE

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Abstract. This article presents the results of kinetic property prediction for low-density polyethylene using the Netzsch Kinetics Neo software, based on differential scanning calorimetry (DSC) data. The kinetic prediction includes a review of thermoanalytical data for chemical processes, process behavior, and temperature optimization. A multi-reaction model approach was applied, incorporating several types of reactions: an n^{th} -order reaction, a diffusion-controlled reaction, an autocatalytic model, and the Avrami–Erofeev model. For each reaction, the activation energy and reaction order were determined, which define the heat flow under specific conditions. The DSC curve shows an endothermic peak at 118 °C, corresponding to the melting point of low-density polyethylene. The prediction of isothermal curves revealed behavior typical of processes governed by an autocatalytic or reaction-diffusion mechanism, where an initial induction period is followed by an increasing reaction rate, rapid heat release, and reaction completion. Isothermal lifetime simulations were conducted at temperatures

ranging from 10 to 160 °C for conversion degrees (α) from 0.02 to 0.8. Additionally, modeling of DSC curves under dynamic conditions at different heating rates (1–16 °C/min) produced DSC peaks that demonstrate the dependence of heat flow on heating rate. Analyzing adiabatic curves at different initial heating temperatures offers insights into the thermal runaway temperature and time, which are vital for assessing material performance in environments without heat loss.

Keywords: differential scanning calorimetry, Netzsch Kinetics Neo, reaction, activation energy, isothermal lifetime, adiabatic curves

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ТӨМЕН ТЫҒЫЗДЫҚТАҒЫ ПОЛИЭТИЛЕННІҢ КИНЕТИКАЛЫҚ ҚАСИЕТТЕРІНЕ БОЛЖАУ ЖАСАУ

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Аннотация. Бұл мақалада төмен тығыздықтағы полиэтиленнің кинетикалық қасиеттерін Netzsch Kinetics Neo бағдарламасы арқылы болжау нәтижелері ұсынылған, ол үшін бастапқы дерек ретінде дифференциалды сканирлеуші калориметрия (DSC) мәліметтері пайдаланылды. Кинетикалық болжау химиялық процестердің термоаналитикалық деректерін, процесс мінез-құлқын және температураны оңтайландыруды қамтиды. Бірнеше реакция түрінен тұратын модельдік тәсіл: n-тәртіпті қарапайым реакция, диффузиямен шектелген реакция, автокаталитикалық модель және Аврами–Ерофеев моделі қолданылды. Әрбір



реакция үшін активация энергиясы мен реакция тәртібі нақтыланып, бұл мәндер белгілі бір жағдайларда жылу ағынын сипаттайтыны анықталды. DSC қисығында 118 °C температурада эндотермиялық шоқы байқалады, бұл төмен тығыздықтағы полиэтиленнің балку температурасына сәйкес келеді. Изотермиялық қисықтарды болжау автокаталитикалық немесе реакция-диффузиялық механизмге тән мінез-құлықты көрсетті: бастапқыда индукция кезеңі байқалып, кейін реакция жылдамдығы артады, жылдам жылу бөлу жүреді және реакция толық аяқталады. Изотермиялық жағдайда материалдың өмір сүру уақыты 10–160 °C температура аралығында, түрлену дәрежелері (α) 0.02-ден 0.8-ге дейінгі мәндер үшін модельденді. Сонымен қатар, әртүрлі қыздыру жылдамдығында (1–16 °C/мин) DSC қисықтарын модельдеу барысында жылу ағынының қыздыру жылдамдығына тәуелділігі көрініс тапты. Әртүрлі бастапқы қыздыру температураларындағы адиабаталық қисықтарды талдау термиялық тұрақсыздықтың температурасы мен уақыты жөнінде ақпарат береді. Бұл материалдарды жылу жоғалуы болмаған жағдайларда қолданғанда маңызды көрсеткіш болып табылады.

Түйін сөздер: дифференциалды сканирлеуші калориметрия, Netzsch Kinetics Neo, реакция, активация энергиясы, изотермиялық өмір сүру уақыты, адиабаталық қисықтар

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ПРОГНОЗИРОВАНИЕ КИНЕТИЧЕСКИХ СВОЙСТВ ПОЛИЭТИЛЕНА НИЗКОЙ ПЛОТНОСТИ

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Аннотация. В данной статье представлены результаты прогнозирования кинетических свойств полиэтилена низкой плотности с использованием программы

Netsch Kinetics Neo, при этом в качестве исходных данных использовались результаты дифференциальной сканирующей калориметрии (DSC). Кинетическое моделирование включает в себя анализ термоаналитических данных химических процессов, поведение процесса и оптимизацию температурного режима. Применён модельный подход, включающий несколько типов реакций: простая реакция n -го порядка, реакция с ограничением по диффузии, автокаталитическая модель и модель Авраами–Ерофеева. Для каждой реакции были определены энергия активации и порядок реакции, что позволяет описать тепловой поток в определённых условиях. На кривой DSC наблюдается эндотермический пик при температуре 118 °С, что соответствует температуре плавления полиэтилена низкой плотности. Прогнозирование изотермических кривых показало поведение, характерное для автокаталитического или реакционно-диффузионного механизма: первоначально наблюдается индукционный период, затем происходит ускорение реакции, интенсивное выделение тепла и завершение реакции. В изотермических условиях смоделировано время жизни материала в температурном диапазоне 10–160 °С при степенях превращения (α) от 0.02 до 0.8. Кроме того, при моделировании кривых DSC при различных скоростях нагрева (1–16 °С/мин) была выявлена зависимость теплового потока от скорости нагрева. Анализ адиабатических кривых при различных начальных температурах нагрева предоставляет информацию о температуре и времени теплового разгона, что является важным показателем при использовании материалов в условиях отсутствия теплоотдачи.

Ключевые слова: дифференциальная сканирующая калориметрия, Netzsch Kinetics Neo, реакция, энергия активации, изотермическое время жизни, адиабатические кривые

Introduction. Polyethylene, as one of the most widely used thermoplastics, plays a critical role across a broad range of industries due to its favorable mechanical properties and chemical stability. However, its thermal decomposition behavior under different heating regimes remains a key concern, particularly in safety-critical applications such as polymer processing, transportation, and storage (Hong et al., 2022). A detailed understanding of its decomposition kinetics is essential for predicting behavior under thermal stress and for designing appropriate thermal hazard mitigation strategies (Li et al., 2012).

Many works are devoted to the investigation of polyethylene. The complex morphology of low-density polyethylene influences the crystallization kinetics and dynamic mechanical properties of the polymers, which are key to the processability and applications (Saalwächter et al., 2023). It is very important to conduct research in the field of crystallization kinetics, crystallinity, lifetime, and thermal properties of this polymer (Poh et al., 2022). Understanding the thermal stability and decomposition mechanisms of polyethylene is essential not only for optimizing manufacturing conditions but also for ensuring safe application in environments where heat exposure is inevitable. Thermal analysis methods play a critical role in this context, with Differential Scanning Calorimetry (DSC) being one of the most widely used techniques. DSC

provides insights into thermal transitions, such as melting and crystallization, as well as more complex phenomena like exothermic degradation reactions. By tracking heat flow as a function of temperature or time, DSC enables the investigation of polymer stability and decomposition kinetics (Alonso et al., 2022).

A particularly powerful application of DSC is under adiabatic conditions, where no heat is lost to the environment. This setup closely simulates real-life scenarios where heat generated by an exothermic reaction is retained within the system, potentially leading to thermal runaway. Adiabatic DSC curves are valuable for identifying key safety parameters, such as the Self-Accelerating Decomposition Temperature (SADT) and the induction time before decomposition onset (Lynch et al., 2024).

In addition to thermal profiling, kinetic analysis is critical for modeling the complex reaction pathways involved in polymer decomposition. Multistep kinetic models, incorporating various reaction mechanisms such as *n*th-order reactions, diffusion-limited steps, autocatalytic processes, and phase transformations, offer a comprehensive approach to describing the thermal degradation behavior of polyethylene. These models help in quantifying important parameters like activation energy, reaction order, and rate constants, providing deeper insight into the material's thermal response under different heating regimes.

Kinetic analysis helps to improve safety standards for handling and storage of energetic materials, predict the behavior of materials under influence of different conditions. Sufficient longevity and good thermal stability are therefore essential (Harter et al., 2022). One of the key importances of this method is the prediction of the material degradation for specific temperature and time conditions. Knowledge of the thermal stability and understanding the decomposition process in the solid state allows for optimizing its storage conditions (Manic et al., 2020)

The study of the kinetics of isothermal crystallization of polyethylene is an active area of research. Numerous studies have been devoted to determining the kinetic characteristics of various types of polyethylene. For example, Patel conducted an extensive investigation of the crystallization kinetics of high-density and linear low-density polyethylene, analyzing changes in the obtained kinetic data depending on the conditions (Patel et al., 2012). These studies showed that the rate and mechanism of polyethylene crystallization strongly depend on temperature, molecular structure, and the presence of comonomers.

Modern methods of thermokinetic analysis not only make it possible to study thermal decomposition and oxidative degradation processes but also to predict the behavior of materials under various temperature conditions. One of the effective tools in this area is the Netzsch Kinetics Neo software, which enables the modeling of reaction kinetics based on thermogravimetric analysis (TGA) data.

The application of kinetic analysis using software such as Kinetics Neo allows researchers not only to explore the fundamental aspects of polyethylene (PE) crystallization but also to address practical challenges. For instance, the work (Harter et al., 2022) demonstrates how isothermal crystallization data of high-density polyethylene (HDPE), obtained via DSC and analyzed using Kinetics Neo, can be employed to

optimize injection molding parameters, highlighting the practical relevance of such analyses (Harter et al., 2022; Manic et al., 2020).

In addition to studies on neat polyethylene, considerable attention is given to modified systems, such as PE-based nanocomposites (Khan et al., 2023). For example, the study (Kourtidou et al., 2021) investigated short-chain branched polyethylene (SCB-PE) modified with graphene nanoplatelets (GNPs). In this work, the (non-isothermal) crystallization behavior and nanomechanical properties of these nanocomposites were examined using DSC. The authors demonstrated that pre-treatment by ball milling improves filler dispersion, significantly affecting the crystallization process and leading to substantial enhancement of the mechanical properties of the composites. This example emphasizes how various factors, including composition and processing methods, can influence the crystallization behavior of polyethylene-based materials.

In another study (Tarani et al., 2024), HDPE-based composites containing tannic acid (TA) were developed. The authors employed DSC to investigate the non-isothermal crystallization kinetics using the Friedman and Vyazovkin methods, as well as the Sbirrazzuoli model. It was shown that the addition of TA influences the crystallization behavior of HDPE: lower TA concentrations promote nucleation, while excessive TA disrupts the ordering of polymer chains and reduces the degree of crystallinity. Furthermore, the addition of TA was found to accelerate the crystallization process of HDPE, as evidenced by a decrease in activation energy values. This study highlights the importance of examining the impact of various additives on the crystallization kinetics of polyethylene and demonstrates the applicability of non-isothermal analytical methods for understanding complex mechanisms.

The decomposition behavior of the polymer was also studied using isothermal and dynamic methods. The isothermal method involves maintaining the sample at a constant temperature over time, allowing precise observation of reaction kinetics under stable thermal conditions. This approach is particularly effective for studying long-term stability, slow degradation processes, and reaction mechanisms with minimal interference from temperature gradients. In contrast, the dynamic method is applied at a controlled heating rate to the sample, capturing the material's thermal response as temperature increases continuously.

This study aims to characterize the thermal decomposition behavior of polyethylene using a combination of the above-mentioned modeling methods. The goal is to better understand the mechanisms governing its thermal degradation and to assess the implications for safety and process control in thermal environments.

Materials and methods

Dynamic Differential Scanning Calorimetry (DSC) analysis was performed using a DSC 300 Caliris® Classic instrument (NETZSCH, Germany) under a nitrogen atmosphere with a flow rate of 40 mL/min to prevent oxidative degradation.

Low-density polyethylene (LDPE) grains supplied by Kazanorgsintez (Russia) were used as the test material. Samples were accurately weighed using a RADWAG® five-digit analytical balance and sealed in NETZSCH Aluminum Concavus® pans using a NETZSCH sealing press. To prevent pressure buildup during heating, a small pinhole

was made in each pan lid. An empty aluminum pan of the same type was used as a reference.

Samples were heated from 30°C to 300°C at a scanning rate of 8K/min. All measurements were conducted under consistent conditions, and thermal events such as melting, crystallization, and degradation were recorded during the heating cycle. NETZSCH Proteus -80(Germany) and NETZSCH kinetics-Neo software (Germany) were used to analyze the collected data and thermal behavior prediction.

Results and discussion

The following graph presents the prediction result using the Multiple Step method, where the X-axis represents DSC (mW/mg) and the Y-axis represents time (minutes)

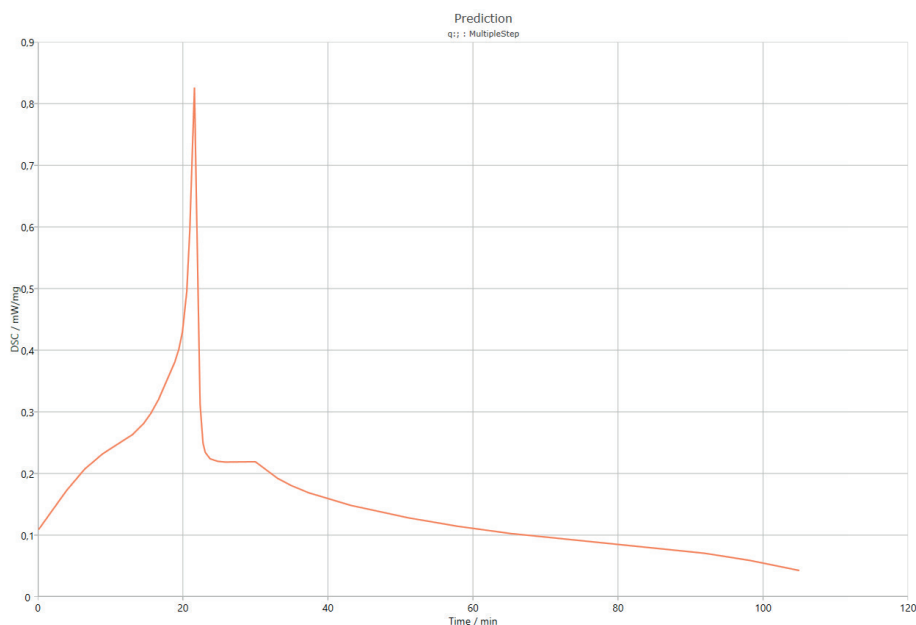


Figure 1. Time-dependent behavior of DSC

The presented graph shows the predicted thermal behavior of the sample using the Multiple Step kinetic model based on DSC data. A sharp exothermic peak is observed at approximately 20 minutes, indicating a rapid and intense reaction phase. The steep rise and immediate drop in the DSC signal suggest that the primary reaction occurs quickly and is highly exothermic, followed by a gradual decline in the DSC signal, suggesting the presence of slower secondary processes such as residue decomposition or delayed structural relaxation.

The shape of the curve aligns well with a reaction mechanism involving multiple overlapping stages, such as initial n-th order reaction kinetics (F_n), diffusion-limited steps (D_3), autocatalytic effects (A_n), and phase transformation processes (C_n). This supports the application of a multistep kinetic model to accurately describe the material's thermal decomposition behavior.

The shape of the curve corresponds to the multi-step reaction model consisting of reactions of F_n , D_3 , A_n , and C_n .

1. F_n — an n-is order reaction, where the reaction rate is proportional to the degree of conversion.

The reaction corresponds to the formula.

$$d\alpha/dt = k \cdot (1-\alpha)^n$$

Where α is the degree of conversion, k is the rate constant, and n is the reaction order. According to the selected model, the reaction order corresponds to 4.3.

2. **D3 — Diffusion model (3D: Jander model).**

This model describes diffusion-controlled processes in solid materials (Wang et al., 2022). The reaction equation is:

$$[1 - (1 - \alpha)^{1/3}]^2 = kt$$

Diffusion of reactants occurs through the reaction product. This stage indicates that the reaction proceeds with the formation of a product that slows down further reaction progress (e.g., hydroperoxides or stable radicals).

3. A_n — **Autocatalytic reaction model** (Zhao et al., 2023)

$$d\alpha/dt = k \cdot \alpha^m \cdot (1-\alpha)^n$$

According to the equation, the reaction starts slowly, then accelerates sharply, and finally slows down.

4. C_{nm} — **Phase growth model (Avrami–Erofeev)** (Duan et al., 2022)

Ultimately, new phases may form in solid materials.

$$\alpha = 1 - e^{[-(kt)^n]}$$

Structured domains may form in the process. The reaction follows a complex mechanism that may involve diffusion limitations, an autocatalytic effect, and phase transformations.

Kinetic parameters of the DSC of polyethylene for each step (reaction) are presented in the following table.

Table 1. Kinetic parameters derived from DSC measurements of polyethylene

	A→B (F_n)	C→D (D_3)	E→F (A_n)	G→H (C_{nm})
Activation energy (kcal/mole)	26.416	79.144	20.434	88.554
Pre-exponential factor	1.185	3.69	-0.788	9.7
Reaction order	4.2		1.032	1.522
Contribution	0.48	0.211	0.219	0.09

Each step is characterized by its activation energy, pre-exponential factor, and reaction order, indicating the complexity of the overall thermal degradation process. The activation energies range from 20.434 kcal/mol (E→F) to 88.554 kcal/mol (G→H), suggesting varying energy barriers associated with different decomposition mechanisms. The highest contribution to the overall process (48%) comes from the A→B (F_n) step, which also exhibits the highest reaction order (4.2), indicative of a complex, multi-molecular reaction. The total apparent activation energy for the polyethylene decomposition is calculated as 41.82 kcal/mol (174.97 kJ/mol), reflecting the weighted contribution of all reaction steps.

Forecast by isothermal curves

On the DSC isothermal curves taken at temperatures from 10 to 160 degrees (Figure 2), different process intensities are observed in the first 3 minutes.

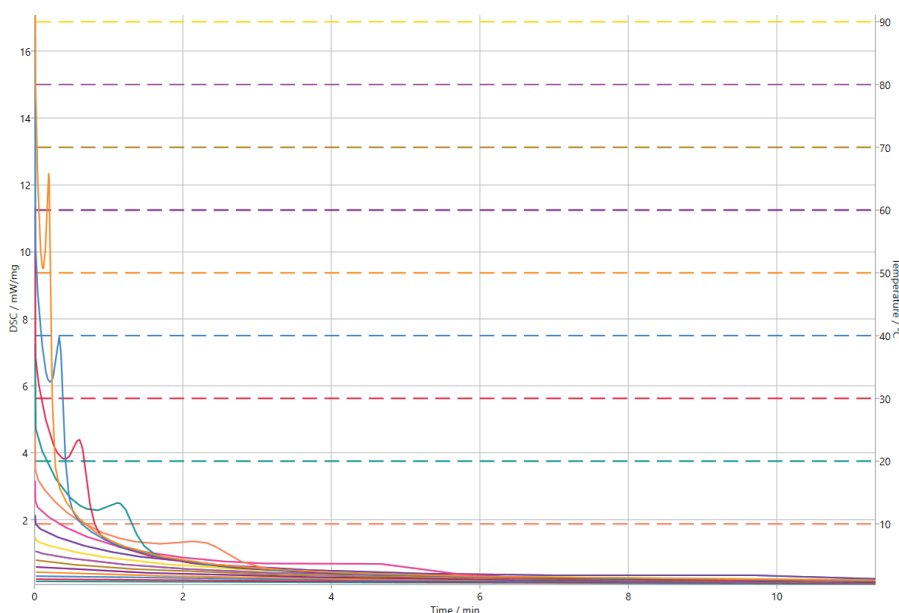


Figure 2. Isothermal curves at various temperatures

As can be seen from the program data, the lower the temperature, the faster the reaction. At temperatures from 10 to 100 degrees Celsius, the DSC isothermal curves do not demonstrate a pronounced exothermic peak, which indicates a slow or insignificant reaction or the reaction rate is so low that it cannot be recorded. Thus, to select the mode of heat treatment of the polymer, polyethylene, you should select temperature values from 100 degrees.

Sharp exothermic peaks appear from 110 degrees. The maximum value of the thermal effect is observed at 160 degrees and is equal to 12.3 mW/mg 0.1 minutes after the start of the reaction, respectively, for the peaks at 150, 140, 130, 120 and 110 degrees these values are equal to - 7.4 mW/mg, 0.3 min., 4.6 mW/mg, 06 min., 2.5 mW/mg, 1.4 min., 1.3 mW/mg, 2.2 min., 0.67 mW/mg, 4.6 min.

That is the time of completion of the complete melting of the sample at 160 degrees. At a temperature of 130 °C, a pronounced exothermic peak is observed with a maximum at 2.5 minutes after reaching isothermal conditions. The maximum thermal power is 1.143 mW/mg, which indicates a high intensity of the ongoing exothermic process (probably a chemical reaction or curing).

The higher the temperature, the faster the crystallization process.

After the peak, the DSC signal drops sharply and reaches a minimum value of 3 minutes, which indicates a rapid progression of the main stage of the reaction. Then the curve gradually levels out, which indicates a slowdown in the reaction and reaching a state close to completion.

Such kinetics is typical for processes occurring by an autocatalytic or reaction-diffusion mechanism, where at the initial stage an induction period with an increasing rate is observed, followed by rapid heat release and completion of the reaction.

Isothermal lifetime

Based on the kinetic model developed using the NETZSCH Kinetics Neo software, an isothermal simulation of the material’s lifetime was conducted at various temperatures ranging from 10 °C to 160 °C, for degrees of conversion from $\alpha = 0.02$ to 0.8 (Figure 3).

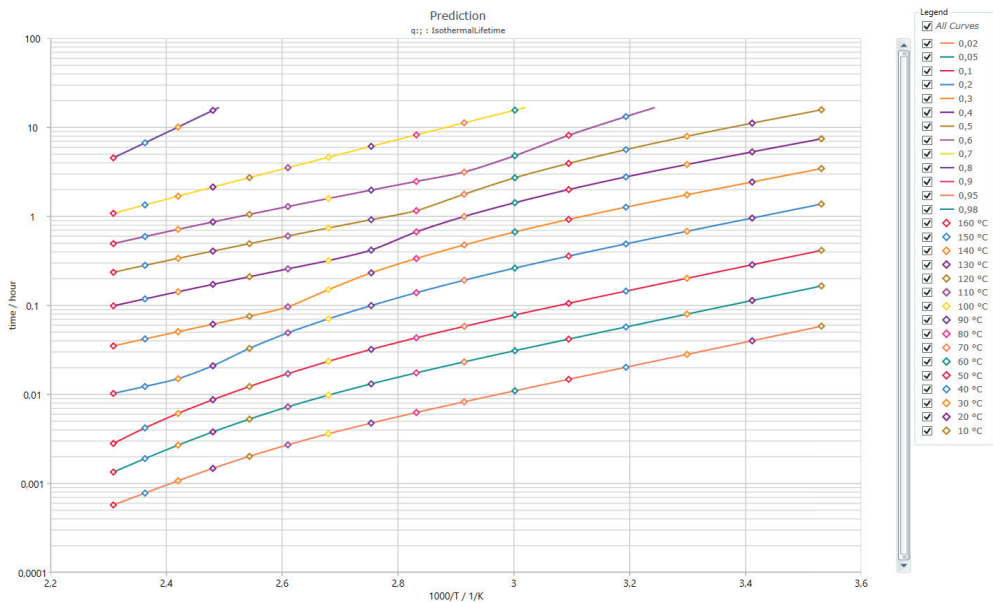


Figure 3. Lifetime curves of polyethylene at different degradation degrees and various temperatures

Here, $\alpha = 0.02$ corresponds to the onset of material degradation, $\alpha = 0.05$ to the loss of functional properties, and $\alpha = 0.8$ to the complete degradation of the material.

The following table shows the time required (in hours) to reach each degree of conversion at different temperatures.



Table 2. Time required to reach the degree of conversion at different temperatures

Temp/°C/ Conversion degree (α)	0,02	0,05	0,10	0,20	0,30	0,40	0,50	0,60	0,70	0,80
160,0	0,001	0,001	0,003	0,010	0,035	0,099	0,236	0,496	1,086	4,561
150,0	0,001	0,002	0,004	0,012	0,042	0,119	0,282	0,595	1,349	6,723
140,0	0,001	0,003	0,006	0,015	0,051	0,143	0,339	0,717	1,691	10,116
130,0	0,001	0,004	0,009	0,021	0,062	0,173	0,409	0,868	2,139	15,561
120,0	0,002	0,005	0,012	0,033	0,076	0,210	0,495	1,057	2,734	
110,0	0,003	0,007	0,017	0,049	0,097	0,258	0,604	1,293	3,535	
100,0	0,004	0,010	0,024	0,071	0,151	0,320	0,742	1,593	4,626	
90,0	0,005	0,013	0,032	0,100	0,233	0,419	0,921	1,978	6,138	
80,0	0,006	0,017	0,043	0,139	0,337	0,672	1,163	2,479	8,261	

The thermal stability of the material was evaluated through isothermal lifetime simulations across a wide temperature range (10°C to 160°C), and the results demonstrate a pronounced temperature dependence of the degradation kinetics. As shown in the figure, the lifetime of the material decreases exponentially with increasing temperature, confirming the Arrhenius-type behavior typically observed in thermally induced degradation processes.

At low temperatures (10–50 °C), the material exhibits relatively long lifetimes for low degrees of conversion. For example, at 10°C, the time required to reach $\alpha = 0.02$ is 0.059 hours, and for $\alpha = 0.05$, it is 0.166 hours. These values correspond to the early onset of degradation and the point at which material properties are notably diminished. The time required for these transitions rapidly decreases as temperature increases: from 9 minutes to 2.5 minutes between 10–50 °C, and further down to 3–25 seconds in the 110–160 °C range. Full degradation ($\alpha = 0.8$) is achieved in just 4.5 hours at 160 °C, while significantly longer times are observed at lower temperatures—15 hours at 130 °C, 10 hours at 140 °C, and 6 hours at 150 °C.

The isothermal lifetime prediction curves in the figure confirm the strong temperature–time correlation. Each curve corresponds to a specific degree of conversion (from $\alpha = 0.02$ to $\alpha = 0.98$), and all show a steep decline in lifetime with increasing temperature. This trend is consistent with the kinetic model's prediction of exponential degradation behavior: the higher the temperature, the faster the degradation occurs.

An especially notable feature in the figure is the appearance of a lifetime minimum of around 640 °C, observed when projecting a total exposure time of 500,000 minutes. This anomaly may suggest a secondary degradation mechanism, such as thermal breakdown with the formation of volatile compounds or pyrolysis, leading to an endothermic effect in the material. As the predicted exposure time is reduced to 100 minutes, this minimum shifts to around 590 °C, reinforcing the concept of temperature–time coupling, where shorter desired lifespans shift thermal instability to lower temperatures.

This behavior exemplifies a fundamental principle in decomposition kinetics:

The longer a material is expected to remain stable, the lower the temperature must

be to ensure its structural integrity. Conversely, even slight temperature increases can dramatically reduce material lifespan if long-term stability is not managed.

Isothermal modulated

The following graph illustrates a modulated isothermal DSC prediction in the temperature range of approximately 119.1 °C to 121 °C.

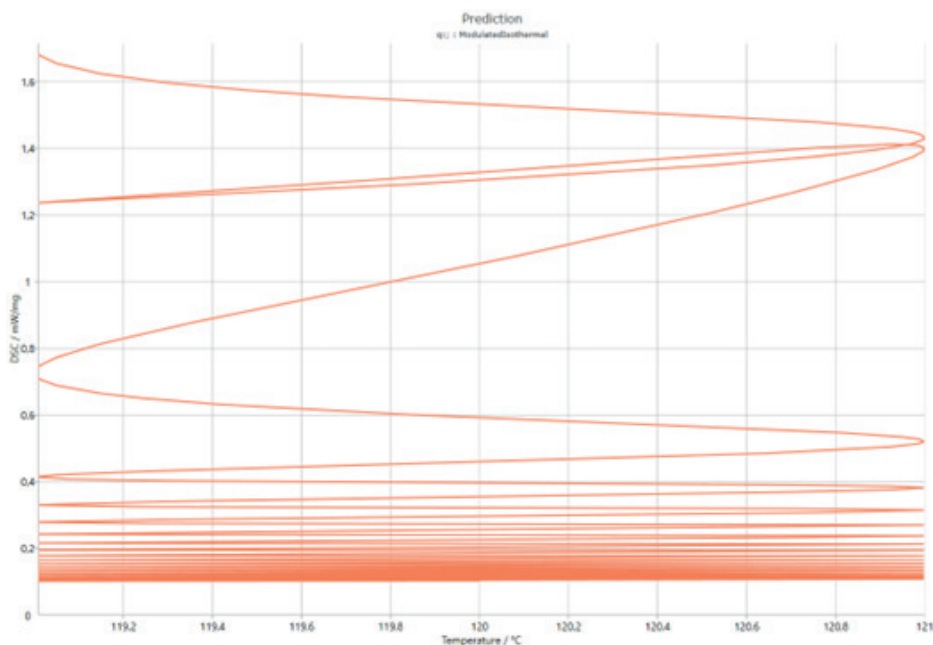


Figure 4. Modulated isothermal DSC prediction

The data reveal distinct oscillatory patterns characteristic of modulated DSC, capturing the dynamic thermal behavior of the material under tightly controlled isothermal conditions.

At lower temperatures (up to ~50 °C), the response remains sinusoidal with low-amplitude fluctuations in the DSC signal (0.08–0.45 mW/mg), indicating relatively stable, reversible thermal processes. However, around 100 °C, this regularity is disrupted, and the heat flow range broadens to approximately 2 mW/mg, suggesting the onset of slower kinetic activity or overlapping transitions. At temperatures beyond 150 °C (not shown here), the amplitude of temperature modulation reportedly decreases, while the DSC response may reach values as high as 18 mW/mg, indicating more intense thermal activity such as degradation.

Within the displayed temperature window (119.1–121 °C), the widening of curves and increasing amplitude, up to ~1.6 mW/mg, suggest nonlinear behavior, possibly due to structural changes or relaxation phase. In contrast, the dense clustering of lower-amplitude curves (~0.2 mW/mg) reflects thermally stable regions with minimal energy exchange.

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Within the displayed temperature window (119.1–121 °C), the widening of curves and increasing amplitude, up to ~1.6 mW/mg, suggest nonlinear behavior, possibly due to structural changes or relaxation phase. In contrast, the dense clustering of lower-amplitude curves (~0.2 mW/mg) reflects thermally stable regions with minimal energy exchange.

Forecast by dynamic curves

The presented DSC data (Figure 5) illustrate the thermal decomposition behavior of polyethylene under dynamic heating conditions, with heating rates ranging from 1 to 16 K/min. The results demonstrate a strong dependence of thermal reactivity on the applied heating rate.

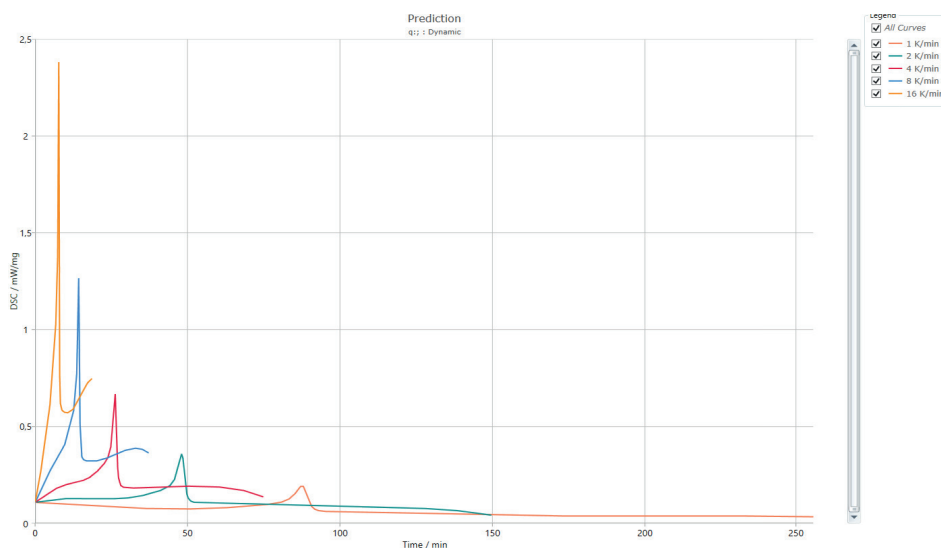


Figure 5. DSC data in the dynamic regime

As the heating rate increases, a shift in peak position and amplitude is observed.

At the lowest heating rate of 1 K/min, the decomposition peak appears at 87 minutes with a relatively low heat flow of 0.19 mW/mg. In contrast, at the highest heating rate of 16 K/min, the peak shifts dramatically to 7.7 minutes, with a significantly higher amplitude of 2.3 mW/mg.

This pronounced shift highlights the kinetic nature of the decomposition process, where increased heating rates lead to a more rapid accumulation of thermal energy, thus accelerating the reaction onset and intensifying the exothermic response.

The table data confirm the thermal shift as the onset temperature increases from 83.7 K at 1 K/min to 99 K at 8 K/min and drops slightly at 16 K/min to 78.4 K, possibly due to overlapping processes or heat transfer limitations. Similarly, the end temperature of the decomposition reaction expands significantly at higher heating rates, from 91.3 K at 1 K/min to 140.8 K at 16 K/min. These changes reflect the non-equilibrium nature of dynamic heating and the limited time for heat dissipation, leading to apparent shifts in the reaction interval with increasing β (heating rate).

Table 2. Onset and end temperatures of reactions

Heating rate (K/min)	Reaction Onset temperature (K)	Reaction End temperature (K)
16	78,4	140,8
8	99	123
4	90,4	110,8
2	91,6	100,8
1	83,7	91,3

Adiabatic prediction

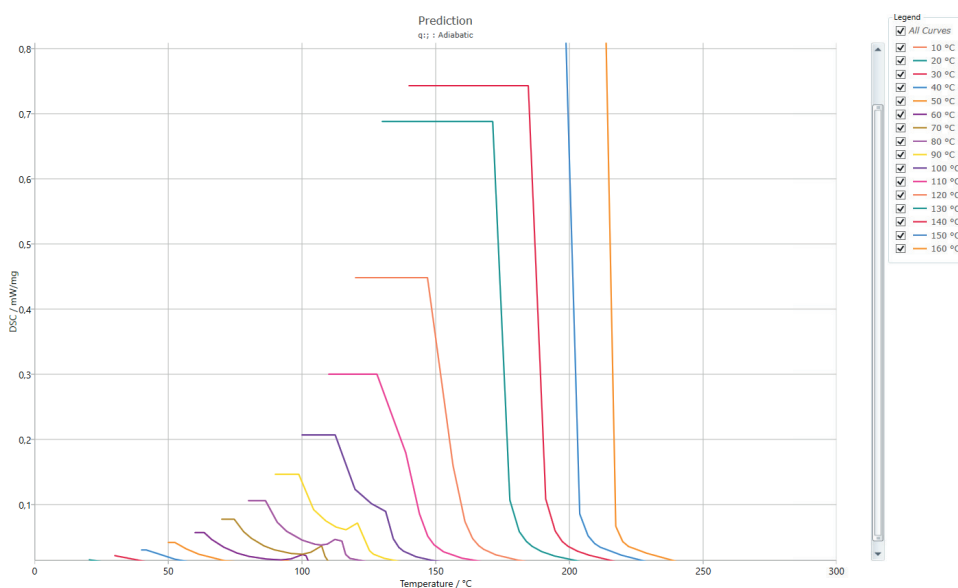


Figure 6. Adiabatic DSC Curves at Varying Initial Temperatures (10°C to 160°C)

The graph shows that as the initial temperature increases, the induction time — the period before observable heat release begins — decreases significantly. This suggests that higher temperatures lower the activation energy barrier for the decomposition reaction, accelerating the onset of self-heating. This behavior is in agreement with autocatalytic thermal decomposition, where the reaction products or intermediates enhance the rate of further reaction.

The system exhibits a strong temperature dependence, indicative of Arrhenius-type

kinetics. The exothermic reaction, likely involving radical chain mechanisms common in polymeric oxidation, becomes increasingly vigorous with temperature, resulting in earlier and sharper heat evolution peaks.

As temperature increases, the rate of heat generation surpasses the rate of heat loss, leading to an uncontrolled temperature rise in an adiabatic environment. This phenomenon poses a serious safety hazard, particularly in industrial-scale polymer processing or storage.

From the adiabatic temperature-time profiles, a critical threshold is evident: around 80°C, a rapid rise in heat flux initiates, marking the onset of self-accelerating decomposition. This aligns with the concept of the Self-Accelerating Decomposition Temperature (SADT), which is a key parameter in the hazard evaluation of reactive materials.

Furthermore, starting from an initial temperature of 120°C, the curves show a plateau or diminished change in thermal behavior, suggesting that the major exothermic reactions have been completed. Beyond this point, thermal stability is regained, and no further chemical transformations significantly contribute to the heat output. This can be interpreted as the system reaching thermal and chemical exhaustion — the depletion of reactive species or the formation of a thermally stable residue.

Conclusion. The complex morphology of low-density polyethylene affects the crystallization kinetics and the dynamic mechanical properties of the polymer, which are important for its processability and applications. Therefore, it is very important to conduct research in the field of crystallization kinetics, crystallinity, lifetime, and thermal properties of this polymer. A multi-reaction model approach was applied to DSC data in the Netzsch Kinetics Neo program, incorporating several types of reactions: an *n*th-order reaction, a diffusion-controlled reaction, an autocatalytic model, and the Avrami–Erofeev model. The total activation energy obtained from the simulation is 41.82 kcal/mol or 174.97 kJ/mol. The DSC curve shows an endothermic peak at 118 °C, corresponding to the melting point of low-density polyethylene.

The prediction of isothermal curves revealed behavior typical for processes governed by autocatalytic or reaction-diffusion mechanisms, where an initial induction period is followed by an increase in the reaction rate, rapid heat release, and completion of the reaction. The isothermal calculation showed that complete degradation of the material is reached in 4.5 hours at 160 °C. At 130, 140, and 150 °C, the corresponding times are 15, 10, and 6 hours. At 10 °C, the material reaches a conversion degree of 0.02 in 0.059 hours and 0.05 in 0.166 hours. This confirms an exponential dependence of the reaction rate on temperature. Modeling of DSC curves at different heating rates (1–16 °C/min) under dynamic conditions showed that the decomposition reaction accelerates with increasing temperature, which is consistent with the mechanism of autocatalytic degradation of polyethylene.

According to the adiabatic prediction, it was found that the higher the starting temperature, the less time is required for the system to reach the maximum heat release — that is, the beginning of decomposition under adiabatic conditions. The maximum power (heat flow) shifts toward higher temperatures. The starting temperature of

thermal runaway was shown to be around 800 °C. These findings highlight the practical value of kinetic modeling and prediction, as they provide critical insights into the thermal behavior and stability of polymers. Such information is essential for optimizing processing conditions, enhancing material safety, and extending the service life of polymer-based products in thermal environments.

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