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*Review Paper*

# Advances in Recycling Process Modeling for CFRPs: A Literature Review

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**Abstract:** Managing large volumes of waste poses a critical environmental challenge, exacerbated by pollution from landfilling and the substantial energy consumption and costs associated with manufacturing specialized materials. Efficient recycling methods play a crucial role in mitigating this impact by facilitating the reuse of components from materials that have not yet reached the end of their life cycle. This challenge is particularly pressing for carbon fiber reinforced polymers (CFRPs), widely used in aerospace applications, for which traditional recycling methods frequently fail to effectively separate composite components or produce recycled materials that meet the stringent specifications required for reuse. This review centers on the theoretical foundations of advanced recycling methods, with a particular focus on the analytical approaches of pyrolysis and solvolysis—two promising techniques for recycling CFRPs. It delves into the dissolution mechanisms of thermosetting matrices, emphasizing fundamental theoretical concepts, kinetic analysis equations, and the role of modeling through various simulation software. The review also highlights critical kinetic parameters such as activation energy and reaction rate constants, which are instrumental in optimizing these recycling processes. Through an integration of analytical calculations, simulation models, and experimental data from the literature, the review evaluates the efficiency and quality of products derived from pyrolysis and solvolysis. This comprehensive approach underscores the importance of modeling in improving the sustainability of CFRP recycling and advancing the development of high-quality, reusable materials.

**Keywords:** Carbon Fiber Reinforced Polymer (CFRP); Thermosetting matrix; Pyrolysis; Solvolysis; Kinetics analysis; Modeling

## 1. Introduction

In recent decades, carbon fiber-reinforced polymer (CFRP) composites have seen substantial use in the aerospace and aeronautics industries because of their outstanding mechanical properties [1]. Thus, they are extensively used in high-performance sports, entertainment, as well as the automotive and aerospace industries, and their applications are rapidly expanding into new areas [2]. The CFRP market is expected to maintain high growth, with projections reaching $20.19 billion by 2028, driven by a compound annual growth rate of 10.1%. This growth is primarily based on the expanding consumer electronics market, the rise of electric vehicles, innovations in CFRP manufacturing, growth in the wind energy sector and advancements in resin systems [3]. While these composite materials provide benefits for aircraft, their distinct physical and chemical characteristics relative to metals present new challenges [1]. The increasing use of CFRP has led to substantial waste disposal issues and environmental pollution. Conventional disposal methods, such as combustion and landfill storage, often worsen these problems and waste valuable resources. Therefore, the study of scientific, environmentally friendly, and economically viable recycling methods of carbon fibers from CFRPs carries significant environmental, social and financial importance [4]. These "waste" materials hold significant inherent value, and the cost of their disposal directly impacts the bottom line for all manufacturers. Consequently, identifying cost-effective solutions for reusing them makes both environmental and financial sense. Previous research has focused on chemically [5,6] and/or thermally degrading the matrix resin to separate the carbon fiber [7]. While thermoplastic composites can often be recycled with minimal degradation of the polymer matrix and reinforcement fibers, thermosetting composites pose greater difficulties due to their cross-linked structure, which complicates recovery without property loss [8]. These issues are strongly linked to the thermal and chemical decomposition behaviors of CFRP at elevated temperatures.

Numerous studies have investigated the pyrolysis behavior of CFRP matrices using Thermogravimetric Analysis (TGA). TGA is a widely used technique for characterizing the thermal decomposition properties of materials. By analyzing thermogravimetric data, researchers can determine kinetic parameters and establish a mathematical relationship—known as the conversion rate equation—between the conversion rate and temperature [1]. Characterization methodologies allow for the determination of basic kinetic parameters, particularly activation energy, which represents the minimum energy required to initiate a chemical reaction. This parameter is influenced by the decomposition state, pressure and temperature, with single-step or multiple-step kinetic models applied depending on the complexity of the decomposition process [9].

To better understand thermal degradation, pyrolysis is defined as a thermal process in which CFRP waste is decomposed in an oxygen-free environment, with or without catalysts. The thermal degradation process of pyrolysis is typically divided into two stages: an initial analysis of CFRP thermal degradation and an investigation into how various parameters affect thermal decomposition behavior. The mass loss of composites during thermal degradation is often measured using TGA instruments, with data collected and recorded via computer. TGA experiments are designed to assess the effects of different atmospheric conditions and isothermal dwelling times, summarizing and comparing the resulting data. This approach allows for the identification of optimal atmosphere conditions, heating rates, and peak temperatures by analyzing the thermal degradation behavior and surface properties of CFRP during pyrolysis [10].

Another approach to matrix dissolution can be described as the thermal motion of atoms, which provides energy for electron transitions. During the electron-hole generation process, electrons escape from covalent bonds in semiconductors, while holes attract electrons and exhibit strong oxidative capabilities. Thermal excitation includes both the surface and bulk excitation of semiconductors. The concentration of carriers (electrons and holes) is directly proportional to temperature; as temperature increases, more electrons transition to the conduction band, generating additional holes. The primary decomposition reaction of CFRP composites involves the fracture and collapse of molecular chains, stemming from the instability of the large molecular chains in the epoxy resin matrix due to the loss of bound electrons. While the concentration of bound electrons cannot be measured directly, it is assumed to be directly proportional to the weight of the resin [11]. Studies have shown that the thermal recycling parameters for different CFRP composite types must be thoroughly adjusted based on the matrix used [10].

The thermo-oxidative degradation of CFRPs is also studied under dynamic temperature conditions. The composites were heated above their glass transition temperature, and the kinetic triplets—activation energy, reaction model, and pre-exponential factor—were derived from TGA and derivative thermogravimetric (DTG) analyses using model fitting, model-free methods, and master plots. These results helped identify the degradation mechanism and assess durability across a wide temperature range. The degradation process was found to be complex, often involving multiple steps. Similar multistep degradation behaviors were observed in other polymeric composites, such as carbon nanotube-reinforced polyolefins and basalt powder-reinforced epoxy composites. Many studies overlooked this complexity, using simplified methods that resulted in a single kinetic triplet that inadequately described the overall degradation. A few investigations account for multistep characteristics, employing non-linear regression to derive multiple kinetic triplets. While mass loss curves were reconstructed for kinetic analysis, this alone does not validate the kinetic parameters, nor does it ensure accurate predictions of degradation under different conditions [12].

In addition, the chemical recycling of CFRP through the decomposition of epoxy resin has been explored using methods like hydrolysis, alcoholysis, hydrogenolysis, nitric acid degradation, and glycolysis. The most significant steps are the decomposition or dissolution of the polymer component in the CFRP and the recovery of undamaged carbon fibers. Techniques involving supercritical and subcritical fluids for polymer recycling have been extensively studied, utilizing water or alcohols as solvents to decompose the thermosetting matrix. Research has also focused on recycling CFRPs with supercritical or subcritical water with or without a catalyst, oxidant, or CO2-expanded water [13].

In recent years, numerous techniques for characterizing the thermal and chemical recycling processes, for CFRPs with thermosetting matrix, have been developed. However, there is a gap for future investigation in how to effectively utilize this data to optimize pyrolysis or solvolysis processes and obtain outcomes. Therefore, gathering studies that focus on process optimization is crucial for advancing the next steps in obtaining more efficient recycling results. This review paper aims to utilize experimental data on the recycling of CFRPs with theoretical models overseeing kinetics and heat transfer. It seeks to develop a predictive model using simulation methods (either analytical or computational) that can help optimize recycling conditions and enhance the quality of recyclates, ultimately saving both time and cost.

## 2. Research Methodology

For such an up to date and crucial subject, it is valuable to gather all the advancements published in the literature and explore ways to continue this research and find improved scientific roots for the recycling of carbon fiber reinforced polymer materials.

This review synthesizes the major achievements in the recycling of CFRP materials, specifically focusing on thermal and chemical recycling methods. Through the collection and analysis of relevant literature, this paper categorizes and evaluates key research on these recycling processes, using analytical methods and simulation modeling.

A comprehensive literature search was conducted from August to November 2024, utilizing several academic databases and research platforms, including ScienceDirect, ResearchGate, MDPI, IOP science, and Google Scholar. The search key words included:

- "Recycling of composite materials"
- "Modeling the Solvolysis/Pyrolysis process"
- "Dissolution of thermosetting matrix"
- "Simulation of Solvolysis/Pyrolysis methods"

In addition to peer-reviewed journal articles, reports and conference proceedings were also considered. The review focused on English-language literature published up to the present (November 2024).

After collecting the articles, each study was screened for relevance based on its title and abstract. The primary steps in the research methodology are as follows:

The first step involved reviewing and analyzing various approaches to recycling composite materials, including mechanical, thermal, and chemical methods. This initial step helped us identify the most relevant approaches for this review. Based on this initial review, we then focused specifically on thermal and chemical recycling, as these methods are more challenging and have greater potential for effectively reusing recyclates.

Next, CFRP materials with thermosetting matrices were chosen for this review due to their widespread use in high-performance industries such as aerospace and automotive. These materials are known for their high toughness and strength, which make them more difficult to recycle compared to thermoplastic composites. Therefore, the review specifically addresses the challenges and advancements in recycling thermosetting CFRPs.

Following this, full-text articles were reviewed to ensure they met the inclusion criteria. The selected studies primarily focused on the thermal and chemical recycling of CFRP materials with thermosetting matrices. By focusing on these materials, this review aims to explore the thermal and chemical recycling processes for CFRPs, particularly by computational models and simulation techniques.

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The modeling approaches were categorized based on their analytical methods and simulation techniques for each type of recycling process, namely solvolysis and pyrolysis. This categorization allowed us to conduct a comparative analysis of the different modeling strategies and their effectiveness in simulating the recycling processes.

The literature data on this subject were analyzed systematically, and a total of 61 studies were included in the final analysis.

## 3. Theoretical Framework

The decomposition of the epoxy matrix can be analyzed by measuring the mass loss of CFRP plates during the pyrolysis process, as described by Equation (1):

$$a = \frac{Mi-M}{Mi-Mf}, \qquad (1)$$

where $a$ is the decomposition degree, $Mi$ and $M$ are the initial mass and the transient mass, respectively, and $Mf$ is the final mass of the sample after pyrolysis.

There are various kinetic approaches, such as iso-conversional methods, model fitting, and the random scission method, examining the pyrolysis process. This section provides a primary analysis of kinetic methods and models, offering a realistic representation of waste plastic degradation [14].

Several Arrhenius-type kinetic analysis methods have been developed by modifying existing equations, with two main approaches: model-fitting and model-free methods. Arrhenius-type kinetics is the mostly used framework for quantifying the thermal decomposition of a number of composite materials. This kinetic method includes three parameters: activation energy, reaction order, and pre-exponential factor. To recover these parameter values, TGA burning profiles of the specimens are utilized. Once TGA data is collected, it can be analyzed using three different methods: multi-curve, single-curve, and peak property methods (PPM). The multi-curve method (implemented by Ozawa, Friedman, and Kissinger) yields values that depend on the degree of decomposition, although errors may arise from neglecting the effect of the heating rate. The single-curve method (used by Coats–Redfern) provides a straightforward model for obtaining parameters, as the choice of reaction order is somewhat arbitrary and not directly tied to the obtained data. Both methods require a curve-fitting procedure for the TGA data. In contrast, the PPM takes advantage of properties at the peak of the derivative thermogravimetry (DTG) curve [15].

The complexity of decomposition varies based on the material being studied. The complex decomposition should be first understood before formulating exact analytical expressions. Empirical homogeneous kinetic expressions are employed to model these mechanisms. Since thermal decomposition is irreversible, it is characterized by a classical reaction rate that follows an Arrhenius equation:

$$\frac{\partial \alpha}{\partial t} = f(a)Aexp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

The various methods for determining the kinetic constants of reactions are all based on the same fundamental theoretical equation derived from the Arrhenius formula, Equation (2), where $T$ is the temperature, $R$ is the universal gas constant, $a$ is the decomposition degree of the material, $f(a)$ is a reaction conversion function, $A$ is the pre-exponential factor and $E_a$ is the apparent energy of activation. Different functions, $f$, exist and correspond to a physical phenomenon. Four categories of functions have been suggested:

1. Diffusion kinetic functions;
2. Phase boundary reaction and reaction order kinetic functions;
3. Nucleation and nucleus growth kinetic functions;
4. Power law nuclear growth functions.

The most commonly used function is based on nth-order reaction kinetics [16]:

$$f(a) = (1-a)^n \qquad (3)$$

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Iso-conversional methods are also used and could be considered among the most reliable approaches for determining activation energy. These methods calculate activation energies by analyzing multiple curves obtained at varying heating rates, while the pre-exponential factor is typically estimated by assuming a first-order reaction model for $f(a)$ over the entire reaction range. The kinetics of solid-state reactions are generally expressed using Equation (4).

$$\frac{dW}{dt} = kf(W), \tag{4}$$

where W is total mass of volatiles released at time t, $k$ is the kinetic rate constant, is assumed to vary with temperature according to the Arrhenius law [14].

A brief overview of each method will be provided, including the differential methods (Friedman) and the integral methos (Kissinger, Flynn-Wall-Ozawa or Ozawa, Kissinger-Akahira-Sunose, Horowitz-Metzger, Starink, Coats-Redfern and Avrami methods). A brief overview of each method will be provided.

The Friedman Method: Taking the logarithm of equation (2) gives the following eq.:

$$\ln\left(\beta\frac{da}{dT}\right) = An(1-\alpha_m)^{n-1}\exp\left(\frac{-E_a}{RT_m}\right), \tag{5}$$

where $\ln\left(\beta\frac{da}{dT}\right) = \ln\left(\frac{da}{dT}\right)$ ,due to the fact that the value $\beta = \frac{dT}{dt}$ and is usually equal to 1.

In the Friedman method, pyrolysis kinetic parameters are determined in two steps. First, for each specific $\alpha$, the activation energy is calculated using the slope of a linear regression plot. From these calculations, the average activation energies corresponding to various conversion levels are derived.

The Kissinger Method: Differentiation on both sides of Equation (2) yields the following equation:

$$\frac{E_a\beta}{RT_m{}^2} = An(1-\alpha_m)^{n-1}exp\left(\frac{-E_a}{RT_m}\right), \tag{6}$$

where $T_m$ is the peak temperature obtained from the DTG curve, $\alpha_m$ ,is the peak conversion corresponding to $T_m$, which is obtained from the TG curve and $\beta$ is the constant heating rate during the experiment. Kissinger considers that $n(1-\alpha_m)^{n-1}$ is independent of $\beta$ and its value is approximately equal to 1. The activation energy $(E_a)$ can be derived from the Equation (6) by taking the logarithm and differentiating.

$$\frac{d\left(\ln\left(\frac{\beta}{T_m{}^2}\right)\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E_a}{R} \tag{7}$$

The thermal weight loss of CFRPs in an inert atmosphere occurs in two primary stages. The connection between the pre-exponential factor $A$, the slope and the intercept of the curve is as follows:

$$\ln\left(\frac{A}{-k}\right) = a \tag{8}$$

When calculating the reaction order $n$, consider the mechanism function to be expressed as Equation (3), and $n$ is calculated by the below equation [16]:

$$-n(1-\alpha_m)^{n-1} = 1 + (n-1)\frac{2RT_m}{E_a} \tag{9}$$

The Flynn-Wall-Ozawa (FWO) Method: The activation energy $E_a$ was computed by the following formula:

$$E_a = -\frac{R}{0.4567}\frac{d(\log(\beta))}{d\left(\frac{1}{T}\right)} \tag{10}$$

The pre-exponential factor was estimated by the following formula:

$$logA = log\beta \ + logE_a + 0.434\left(\frac{EA}{RT}\right) - \ logR - 2logT \tag{11}$$

At the same degree of conversion, the corresponding pre-exponential factor values were calculated for various heating rates, leading to the determination of average values.

The Horowitz-Metzger method: this method is a novel mathematical approach to interpreting thermogravimetric data that allows for the convenient determination of kinetic parameters in pyrolysis reactions. By plotting a function of the remaining weight fraction against temperature, the activation energy can be derived from the slope of the resulting straight line. The close agreement between the activation energy values obtained using this method and those reported in the literature for various polymers confirms the validity of this approach [17].

$$\ln\left(ln\frac{W_i-W_f}{W-W_f}\right)) = \frac{E\Theta}{E{T_s}^2}, \tag{12}$$

where, $T_s$ is the reference and about the variable $\Theta$ applies that: $T = T_s + \Theta$, with $T$ the current temperature.

The Avrami method: this method is a kinetic model used to describe phase transformation processes. It explains the relationship between the transformed fraction of material and time, accounting for growth of new phases. This method is especially useful in isothermal and non-isothermal conditions. The Avrami equation is expressed as:

$$X(t) = 1 - \exp\left(-Kt^n\right), \tag{13}$$

where, $X(t)$ is the proportion of material transformed at a given time, $K$ is the transformation rate constant, $t$ is the time and $n$ is the Avrami exponent, which provides insight into the nucleation and growth behavior [18].

Coats–Redfern Method: Coats and Redfern assumed the function of the kinetic mechanism is same as Kissinger Method Equation (6), and derived the following expression:

$$\ln\left(\frac{\alpha}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right)\left[1 - \left(\frac{2RT}{E_a}\right)\right] - \left(\frac{E_a}{RT}\right), \tag{14}$$

In the logarithmic term on the left side of the equation, the result comes from integrating $1/f(\alpha)$ and neglecting higher-order terms under the assumption of a low conversion rate after polynomial expansion. To investigate the kinetic model of thermal decomposition, assuming the mechanism function is unknown, the alternative term in the logarithmic expression is the integral form $F(\alpha)$ of $1/f(\alpha)$. Additionally, considering that $\frac{2RT}{E_a}$ approaches zero, the formula is as follows [16]:

$$\ln\left(\frac{F(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_A}\right) - \left(\frac{E_a}{RT}\right) \tag{15}$$

The Kissinger-Akahira-Sunose Method: KAS is another integral method which determines the activation energy of a reaction by analyzing data obtained at different heating rates, without assuming a specific reaction model. The basic equation that is used for any specified $\alpha$ is [19]:

$$\ln\left(\frac{\beta}{T^2}\right) = const. - \frac{E_a}{RT} \tag{16}$$

The Starink method: this method follows the same approach as that of KAS method but redefines some preliminary assumptions, based on the experimental results of solid-state thermal decomposition reaction. The Starink method provides a highly accurate approach for calculating activation energies from constant heating rate experiments, it minimizes errors and delivers reliable results across various heating rates and reaction conditions, making it ideal for complex thermal analyses [20].

$$\ln\left(\frac{\beta}{T^2}\right) = const. - \frac{1.007E_a}{RT} \tag{17}$$

Moreover, model fitting involves calculating kinetic parameters based on an assumed reaction model that describes the relationship between conversion and reaction rate. These methods aim to minimize the disagreement between experimental reaction rate data and calculated values, typically using nonlinear regression techniques. Employing models fitting across various temperature programs can help analyze even complex reaction mechanisms [14]. The kinetic theory of distributed activation energy model (DAEM) assumes that the entire process consists of an infinite number of parallel first-order reactions, each with its own activation energy. To represent the distribution of activation energies, the Gaussian distribution function is commonly used, featuring a mean value and standard deviation. The activation energy $E_a$ and pre-exponential factor $A$, for a specific conversion, can be determined from the slope and intercept of the plot of:

$$In\left(\frac{\beta}{T^2}\right) = f\left(\frac{1}{T}\right) \tag{18}$$

The Miura-Maki method is recommended for standard DAEM, as it is typically challenging to define the $A$ as a fixed value in the context of complex pyrolysis. Furthermore, the multi-DAEM is taken as the weighted sum of each single DAEM with individual activation energy distribution $f_j(E)$. The global $f(E)$ is a weighted sum of individual $f_j(E)$ in each reaction, as expressed in Equation (18). Therefore, the overall $\frac{d\alpha}{dT}$ curve can be given as a weighted sum of each individual $\frac{d\alpha}{dT}$ curve, as expressed in Equation (19).

$$f(E) = \sum_1^n c_j f_j(E), \tag{19}$$

$$\frac{d\alpha}{dT} = \sum_1^n c_j \frac{d\alpha_j}{dT}, \tag{20}$$

where $n$ is the number of the individual $f_j(E)$, and $c_j$ represents the weighted contribution of the overall degradation process, and it varies from 0 to 1 [21].

On the other hand, chemical recycling is carried out by adjusting the concentration and reaction time of the solution to optimize the depolymerization conditions. The degree of depolymerization of the epoxy resin was determined using the following equation. [22].

$$DDEP = \left(\frac{DWEP}{TWEP}\right) \times 100\%, \tag{21}$$

where, $DWEP$ is the difference between the CFRP weight before and after the reaction and $TWEP$ is calculated by multiplying the epoxy resin content of CFRP by the weight of the CFRP.

The findings may suggest that the depolymerization kinetics of cured epoxy resin ($EP$) can be described as a pseudo-first order reaction and the depolymerization kinetic equation of cured EP can be simplified.

$$\frac{d[EP]}{dt} = k[EP][mCPBA]^m[DCM]^n, \tag{22}$$

In Equation (21), $mCPBA$ (meta-chloroperbenzoic acid) and $DCM$ (dichloromethane) represent their concentrations [23]. If we assume that both $mCPBA$ and $DCM$ are added in excess and their concentrations remain constant throughout the reaction, we can integrate Equation (21) to represent the change in the amount of decomposed as a function of time, as illustrated in Equation (22). The initial amount of $EP$ is expressed as $[TWEP]$, while the amount of $EP$ remaining after a specified time is represented as $[ResidueEP]$.

$$ln\frac{[ResidueEP]}{[TWEP]} = -k't \tag{23}$$

The expression for $\frac{[ResidueEP]}{[TWEP]}$, denoted as $\frac{a-x}{a}$, utilizes the weights of a specific time interval ($ResidueEP$) and the initial weight ($TWEP$), where $-x$ represents the weight at a given time interval, and $a$ is the initial weight. The negative slope of the line, between $ln\frac{[ResidueEP]}{[TWEP]}$ and reaction time, is indicative of a key characteristic of the solvolysis reaction [24].

Additionally, to enhance our understanding of the experiments that provide data for kinetic analysis, we will briefly explore some fundamental tests, including Thermogravimetric Analysis (TGA), Gas Phase Analysis, and other relevant methodologies.

Firstly, TGA was conducted using TA Instruments. The balance purge flow is carefully calibrated to a specific rate, while the sample purge flow is increased with nitrogen. The thermal decomposition behavior of CFRP samples is examined in various atmospheres ($N_2$, air, $CO_2$, and $H_2O$) at different heating rates, reaching impressive temperatures of up to 1000°C. The TGA results are crucial for calculating the pyrolysis kinetics of the epoxy resin. From the TGA results, key parameters are derived, such as decomposition activation energy, integral procedure decomposition temperature, polymer decomposition temperature, and maximum pyrolysis temperature. Calculating the pyrolysis activation energy allows to optimize the conditions for the epoxy resin, using TGA across various atmospheres [25].

In the context of Gas Phase Analysis, a Fourier Transform Infrared (FTIR) spectrometer is employed to characterize the gases released during decomposition. This FTIR spectrometer was integrated with the TG device, enabling gases emitted from the material to flow through a heated transfer line before reaching the FTIR. The transfer line is maintained at a temperature exceeding 200°C to prevent gas condensation, and the infrared spectra is recorded with great care [9].

In addition to TGA and FTIR, we can utilize other methodologies to collect kinetic data, such as X-ray Photoelectron Spectroscopy (XPS), which is particularly useful for investigating chemical changes in carbon fibers (CF) and recycled carbon fibers (r-CF) and Scanning Electron Microscopy (SEM) that is employed to study the morphology of samples in detail. Besides, tensile tests are performed on virgin carbon fibers (v-CF) and r-CF to measure their tensile strength and Young's modulus, using a single-fiber tensile tester for precision. Pull-out tests are conducted to assess the interfacial fiber strength (IFSS) of single CF composites. Also, to measure electrical conductivity, we secure a single CF at both ends with silver paste and quantified resistance using an ohmmeter; conductivity was calculated based on the shortest length. We repeated this process for both v-CF and r-CF samples. To evaluate the contact angle, a high-resolution camera is installed in the embedding system, capturing the angle at the interface between the CF and the resin. Additionally, a Proton Nuclear Magnetic Resonance (NMR) Spectroscopy and a thermal analyzer are employed to assess thermal conductivity, thermal diffusivity, and volumetric heat capacity. Finally, High-Performance Liquid Chromatography (HPLC) is used for supplementary analyses [24].

## 4. Analytical and Computational Perspectives on CFRP Recycling

### *4.1. Analytical Insights into CFRP Recycling Techniques*

#### 4.1.1. Analysis of the Pyrolysis Process

The analysis of thermal dissolution can be conducted using various methods. The Arrhenius law serves as the basic framework for optimizing chemical reactions. The two major types of Arrhenius-based approaches used in thermal analysis are model-fitting and model-free methods. For the model-free methods, four Arrhenius-type model-free methods are mainly used: the Friedman, Kissinger-Akahira-Sunose (KAS), Flynn–Wall Ozawa (FWO) and Starink method. On the other hand, for the model-fitting methods, the Coats-Redfern curve fitting method is the most common. Most of the studies analyze thermal recycling with more than one method and compare the results to determine which method is most suitable for the specific conditions of pyrolysis.

There are several studies that focus on deriving or estimating the kinetic parameters (activation energy, pre-exponential factor, reaction order, etc.) based on various methods:

A study [26] focused on the pyrolysis behavior and reaction kinetics of the epoxy resin matrix in CFRPs using cone calorimetry and thermogravimetry. The pyrolysis process occurs in three stages: two involving the decomposition of the epoxy resin matrix and one involving the decomposition of carbon fibers. The heating rate significantly affects the pyrolysis process, with an increase in heating rate shifting the temperature of the maximum weight loss rate to higher temperatures. The apparent activation energies determined using the Kissinger and Flynn-Wall-Ozawa methods were found to be consistent, indicating high thermal stability of this epoxy resin matrix. However, its thermal stability does decrease under certain conditions. Among the materials studied, carbon fiber/epoxy laminates were identified as the most prone to pyrolysis. At the same temperature, the carbon fiber/epoxy prepreg exhibit-ed the least weight loss, while the carbon fiber/epoxy laminate showed the greatest weight loss.

In [19], to enhance the recovery quality and economic viability of reclaimed fibers, a kinetic analysis of the thermal decomposition of CFRP was conducted. The study examined the thermal degradation behavior of CFRP up to temperatures of 800°C using a thermogravimetric method to track the decomposition of samples during pyrolysis. The decomposition process was divided into two stages, with the majority of the polymer matrix (55%) being re-moved in the first stage. Kinetic analysis of the resin matrix degradation was carried out using five different models: four model-free Arrhenius-type methods (Friedman, FWO, KAS, and Starink) and one curve-fitting method (Coats-Redfern). The goal was to determine the activation energy at each pyrolysis stage to minimize fiber surface damage and energy consumption during CFRP thermal decomposition. In stage one, reducing the heating rate improved the conversion fraction and minimized energy input. For stage two, an optimized heating rate of around 20°C/min was found to be most effective. However, because stage two was less efficient in matrix degradation and stage one alone couldn't produce high-quality recycled carbon fibers, an oxidation method was integrated into the recycling process. The results demonstrated that pyrolysis up to 425°C, followed by oxidation at 550°C with a heating rate of 10°C/min and a specific isothermal dwelling time, produced clear recycled carbon fibers with minimal surface damage.

In [27], the thermal degradation of CFRP was analyzed by studying the weight loss and determining the activation energy ($E_a$) of the composites using both the Friedman method and the Coats-Redfern method. The Friedman method involves a differential kinetic analysis to evaluate polymer decomposition by plotting data from various heating rates at the same decomposition degree, allowing for the determination of kinetic parameters. $E_a$ is calculated by multiplying the slope of the trend line by the negative gas constant ($R$). The Coats-Redfern method is used to assess the effect of heating rate on activation energy. The thermal degradation of CFRP follows a two-stage reaction with nonlinear parabolic behaviour, requiring the process to be divided into smaller sections before applying the Coats-Redfern method. The activation energy determined using the Friedman method shows that $E_a$increases up to 50% conversion of the epoxy matrix. Between 60% and 80% conversion, a lower $E_a$ indicates a transition in the reaction, while a higher $E_a$ suggests that additional energy is needed to degrade the remaining matrix and pyrolytic carbon. The results reveal that approximately 75% of the epoxy matrix is removed during the first stage of decomposition. Kinetic analysis further confirms that a lower heating rate leads to a higher conversion rate and lower activation energy.

In [10], building upon their previous research, the authors recommended optimal heating temperatures and operating parameters (such as atmosphere, heating rates, and isothermal dwelling time) through an analysis of the kinetic behavior of CFRP thermal degradation. The goal was to obtain clean, undamaged recycled fibers while minimizing energy consumption. Two main Arrhenius-based methods were used: model-fitting and model-free (FWO). The integral multi-curve approach was found to accurately estimate the kinetic parameters of single-step processes, leading to the conclusion that the heating rate significantly influences the reaction behavior. The evaluation of the activation energy profile aligned with established literature, and the kinetic behavior analysis demonstrated that both low and high heating rates achieved high efficiency in resin degradation.

In [28], the thermal degradation behavior and reaction mechanism of CFRP were studied using thermogravimetry combined with Fourier transform infrared spectrometry at varying heating rates. The researchers concluded that the fourth-order reaction model governs the pyrolysis of CFRPs. They employed the FWO and KAS methods to assess the kinetics. The study observed a kinetic compensation effect under different experimental conditions, such as varying heating rates, reaction atmospheres, and kinetic models. The activation energy increased with higher heating rates. The activation energies calculated using the FWO method ranged from 206.27 to 412.98 kJ/mol, with an average of 274.97 kJ/mol, while the KAS method yielded values from 206.51 to 422.85 kJ/mol, with an average of 278.21 kJ/mol. Comparing the activation energies estimated by the Coats-Redfern method with those predicted by the KAS and FWO methods, the study confirmed that the fourth-order reaction model is responsible for the pyrolysis of the carbon fiber epoxy composite.

In [29], a variety of composite wastes were pyrolyzed in a bench-scale, static-bed reactor at temperatures ranging from 350°C to 800°C. The product mass balance and gas composition were found to depend on the polymer matrix, pyrolysis temperature, and, at higher temperatures, the decomposition of thermally unstable fillers present in certain samples. The same waste samples were also pyrolyzed in a thermo-gravimetric analyzer, and the Arrhenius kinetic parameters for the main decomposition reactions were determined using a non-isothermal method. The total weight loss during the pyrolysis and oxidation stages was calculated as a percentage of the sample's initial weight. The kinetic parameters, including apparent $E_a$, preexponential factor ($A$), and reaction order ($n$), were calculated for each major DTG peak, where DTG curve, or derivative thermogram, represents the rate of weight loss of a sample as a function of temperature or time, highlighting the points of maximum decomposition during pyrolysis or oxidation. While pyrolysis is typically assumed to follow a first-order reaction with respect to the amount of decomposable material remaining, composites with phenolic and epoxy resin matrices continued to lose mass steadily even after polymer decomposition had ceased. This ongoing mass loss may be associated with the carbonization of the remaining solids.

In [1], the thermal decomposition characteristics of CFRP composites were analyzed, enabling accurate predictions of their behavior under various temperature conditions. Kinetic analysis was performed in a nitrogen atmosphere, leading to the development of an enhanced pyrolysis prediction model suitable for arbitrary temperature programs. Different approximation techniques, including FWO, Kissinger–Akahira–Sunose, and Starink methods, resulted in distinct equation forms. Once the activation energy and reaction model were identified, the Málek method was applied to determine the pre-exponential factor. The kinetic analysis focused on defining the relationship between the conversion rate and temperature by addressing the kinetic triplet. Although variations were observed in the kinetic parameters obtained through different iso-conversional methods (KAS, FWO, Starink, and Friedman), all methods effectively described the thermal decomposition behavior of the material. The findings revealed that decomposition begins at 227°C, with the peak weight loss rate occurring between 377°C and 477°C, depending on the heating rate. The thermal decomposition under a nitrogen atmosphere can be represented as a single-step reaction, and multiple iso-conversional approaches are applicable for calculating the kinetic parameters.

In [30], the thermo-chemical degradation of CFRPs exposed to intense heat fluxes were investigated. The study integrated heat diffusion, polymer pyrolysis, associated gas production, and convection through partially degraded CFRPs. The aim was to establish the reaction kinetics necessary to model polymer degradation, assuming a temperature-dependent reaction. Parameters such as the activation energy, pre-exponential factor and the reaction order were determined using the Arrhenius equation. The findings identified $E_a$ as $181.73 \times 10^3$ J/mol, $A$ as $3.15 \times 10^{11}$ $s^{-1}$, and $n$ as 1.344. In addition to pyrolytic decomposition, the epoxy and carbon fibers were noted to undergo phase transitions. However, no equation was required for carbon fibers, as they were assumed to remain chemically inert. Experimental validation of the study's assumptions and input parameters demonstrated its effectiveness in accurately modeling both polymer pyrolysis and the high gas pressures generated during decomposition both polymer pyrolysis and the high gas pressure produced in such a decomposition.

The work of [16] analyzed a CFRP product to determine its thermal degradation mechanism and identify pyrolysis products using simultaneous thermal analysis, Fourier transform infrared spectroscopy, and mass spectrometry. A kinetic model was developed, with kinetic parameters calculated using the Kissinger differential method, the Friedman differential method, and the Ozawa integral method. These methods provided activation energy without requiring prior knowledge of the material's degradation reaction mechanism. The Kissinger method assumes the maximum reaction rate occurs at the peak temperature, the Friedman method assumes the reaction kinetic constant, activation energy and the reaction degree are independent of heating rate, and the Ozawa method assumes constant conversion at the peak temperature across different heating rates.

Additionally, the Coats–Redfern method was employed to determine the reaction mechanism function. The study revealed that thermal degradation proceeds in three steps under an inert atmosphere but in four steps under an air atmosphere. The first two steps are similar in both conditions, involving drying, carbon dioxide release, and epoxy resin decomposition. In the third step under an inert atmosphere, phenol is generated, methane levels decrease, carbon monoxide nearly disappears, and carbon dioxide production increases.

The following studies emphasize the use of oxidation processes or supercritical fluids for the degradation or recycling of CFRP composites:

In [31], reaction kinetics models for CFRP degradation in supercritical fluids by examining the chain scission reactions within the cross-linked network were developed. The study explored how reaction time and temperature influence the residual resin content on recycled carbon fibers. Reaction kinetics equations for CFRP degradation in various supercritical fluids were proposed. The degradation of epoxy resin in CFRP was primarily attributed to the scission of linear chain segments and cross-linked segments, particularly C–N bonds in the curing system. Since the concentration of cross-linked bonds cannot be measured directly, parameters $k$ and $n$ were estimated using the Levenberg–Marquardt method and a universal global optimization algorithm, based on resin weight ($W_{resin}$) over time ($t$). Nonlinear fitting of experimental data ($t,\ W_{resin}$) was performed to determine nn, with curves optimized to match experimental conditions. The temperature dependence of $k$ followed the Arrhenius equation, and it was found that the $n$ value for degradation in supercritical methanol was larger than in other fluids, generally ranging from 2 to 3. The study concluded that supercritical methanol and isopropanol are not suitable for CFRP degradation. Building on this, [32] established a kinetic model for the decomposition of epoxy resin and proposed a method to solve kinetic parameters during the recycling of high-performance carbon fibers (CFs), using thermal excitation of a $Cr_2O_3$ semiconductor. The effects of temperature and treatment duration on the epoxy resin decomposition rate were analyzed. The primary decomposition mechanism involved the fracture and collapse of molecular chains, stemming from the instability of large epoxy resin molecular chains caused by the loss of bound electrons. Experimental data ($t,\ W_{resin}$) fitted using nonlinear optimization methods, including the Levenberg–Marquardt algorithm. By comparing optimized and condition-fitting curves, $n$ and $k$ were determined, and $k$ was found to depend on temperature according to the Arrhenius equation. For simplification, $n$ was approximated as 1.5, with the activation energy and pre-exponential factor calculated as 85.03 kJ/mol and $1.26\times10^{6}$ $min^{-1}$, respectively. The kinetic equation effectively predicts changes in $W_{resin}$ during recycling, addressing uncertainties in temperature and treatment time. Furthermore, recycled CFs processed at 480°C for 30 minutes achieved tensile strength 102.72% of the original CFs, suggesting successful surface heat treatment during recycling.

In [33], a pyrolysis method was employed to recycle CFs from CFRPs, followed by oxidation to eliminate residual pyrolytic carbon. DFT calculations were utilized to examine the mechanism underlying the oxidation of pyrolytic carbon, offering theoretical insights into the recovery process of carbon fibers from CFRPs. The effects of oxidation temperature, time, and oxygen concentration on the properties of the r-CFs were evaluated using the response surface methodology. Under optimal conditions, the recycled CFs achieved a tensile strength of 96.2% compared to virgin CFs (v-CFs), a tensile modulus exceeding that of v-CFs, and a recovery rate of 95.2%. The study revealed that the adsorption energy of oxygen on pyrolytic carbon and the activation energy for its reaction were lower than those for carbon fibers, demonstrating that pyrolytic carbon oxidizes more readily than the carbon fibers themselves.

In [21], the oxidative pyrolysis behavior of epoxy resin from fiber/epoxy composites was investigated using a thermogravimetric apparatus and a fixed-bed reactor. A multi-distributed activation energy model (multi-DAEM) was developed to analyze the oxidative pyrolysis kinetics of epoxy resin under different atmospheric conditions. This model assumes the overall process consists of an infinite number of parallel first-order reactions, each with a distinct activation energy. To determine the kinetic parameters ($A,\ E_a$, and standard deviation $\sigma$), a simplified equation proposed by Miura and Maki was utilized. This approach requires experimental data from three different

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heating rates, and the calculated results closely matched the experimental observations. These findings confirmed that the multi-DAEM method effectively models and predicts the oxidative pyrolysis kinetics of epoxy resin. The average activation energy for epoxy resin pyrolysis was found to range between 130–230 kJ/mol, corresponding to three main first-order reactions. In an air atmosphere, $E_a$ values calculated by the multi-DAEM method varied from 76.2 to 327.1 kJ/mol, consistent with those obtained through the Miura-Maki method. The study also highlighted that the degradation behavior of epoxy resin was strongly influenced by oxygen concentration. Higher $O_2$ levels significantly accelerated the primary decomposition of the resin and the oxidation of residual material at lower temperatures.

In [34], the oxidation behavior of a toughened epoxy resin reinforced with carbon fibers was analyzed under both kinetic and mixed thermal-diffusive regimes. Thermogravimetric measurements identified three main reaction stages during oxidation. The first stage occurs between 223°C and 457°C and involves the oxidative decomposition of the resin. This stage is characterized by a reaction with an activation energy of 82 kJ/mol. The second stage involves the oxidation of resin char, which concludes around 577°C. This process follows global kinetics with an activation energy of 105 kJ/mol. At higher temperatures, the oxidation of carbon fibers occurs, described by global kinetics with an activation energy of 184 kJ/mol. Weight loss profiles from the thermogravimetric analysis revealed key stages in the oxidation process. The first stage comprises at least two distinct steps: the oxidative decomposition of the resin, which generates volatile species and char, followed by the further devolatilization of the produced char. The second stage corresponds to the oxidation of the char formed during the initial degradation of the resin. These findings provide a detailed understanding of the composite material's behavior during oxidation.

In [35], a one-step kinetic model for epoxy pyrolysis, developed through TGA was proposed. To estimate the activation energy $E_a$, Friedman's method was applied, which enables the determination of the number of reactions by examining the variation of $E_a$ with the conversion rate $a$. This method allows for analysis across different heating rates, where lines connecting constant $a$ values at varying rates can be plotted. Kinetic parameters derived from this single-reaction mechanism showed excellent alignment with both experimental data and previous literature findings. The study identified three distinct thermal degradation stages:

1. Thermal Desorption (T ≈ 300°C): Only thermal desorption processes occur at this temperature;
2. Depolymerization (300°C < T < 600°C): Degradation is dominated by the scission of epoxy monomer units. This stage primarily releases water and bisphenol as the main degradation products;
3. Fragmentation (T > 600°C): Further fragmentation of the epoxy monomer takes place, leading to the release of larger quantities of permanent gases.

These findings contribute significantly to understanding the thermal degradation behavior of CFRP materials, with a primary focus on insights gained through thermo-gravimetric analysis. Such studies are essential for advancing knowledge about CFRP performance under thermal conditions.

In [25], an energy-efficient recycling method for CFRPs using various reactive gases and controlled pyrolysis periods was developed. The study included an analysis of the activation energy of polymer matrix decomposition to determine optimal pyrolysis conditions based on the type of reactive gas. A two-step pyrolysis process was implemented to eliminate all carbonaceous residue, with effective carbon fiber recycling achieved after 40 minutes of treatment in superheated steam. The recycled carbon fibers retained over 80% of the strength of virgin fibers. TGA was employed to conduct a detailed thermal analysis using the Integral Procedure Decomposition Temperature (IPDT) to assess the thermal properties during the decomposition of epoxy resin. Results showed that steam provided the lowest thermal stability index for the epoxy resin, making it the most effective pyrolysis gas for this process. The activation energy of pyrolysis was calculated using Kissinger's equation, which helped optimize pyrolysis conditions, reducing processing times and leading to the development of an energy-saving recycling process.

In [36], the activation energy of pyrolysis was investigated using the Coats–Redfern (CR) and Flynn–Wall–Ozawa (FWO) methods. The CR method focused on the kinetics of the primary pyrolysis stage, demonstrating that $E_a$ decreased with increasing heating rates and higher proportions of epoxy resin in the mixture. In contrast, the FWO method examined the overall process, indicating that $E_a$ varied across different stages. Analysis across three heating rates showed that $E_a$ decreased as the epoxy resin content increased. Both methods corroborated these findings. The study also revealed that carbon fibers influenced $E_a$. Specifically, pure epoxy resin exhibited lower activation energy compared to epoxy/carbon fiber blends. TG–FTIR analysis provided additional insight into the thermal decomposition mechanism by tracking variations in gas products with temperature. The FWO method identified three distinct phases in the pyrolysis process based on conversion rates, with the lowest $E_a$ occurring during the peak pyrolysis stage. These results contributed to a deeper understanding of the pyrolysis behavior of epoxy resin and its composites.

In [15] a comprehensive investigation into the thermal decomposition kinetics of CFRPs to determine parameters such as $E_a$, $n$ and $A$ was conducted. Techniques like TGA and Differential Scanning Calorimetry (DSC) were employed. As with many reaction kinetics studies, the rate constant was expressed as a function of temperature via the Arrhenius equation. For $E_a$ calculation, the Flynn and Wall method was used, while the try-and-error method was applied for $n$ estimation. The study explored various kinetic analysis methods, including the modified Peak Property Method (PPM), Coats and Redfern, Kissinger, Friedman, and Ozawa methods. Pyrolysis experiments with composite materials were conducted at different heating rates using TGA. Results indicated that the modified PPM outperformed other methods in predicting experimental data. This approach avoided curve fitting and iterative computations, simplifying the analysis by eliminating the need for complex programming to solve nonlinear equations. Furthermore, the modified PPM accurately fits experimental data across all tested heating rates, highlighting its efficiency and reliability.

In [12], the thermo-oxidative degradation behavior and kinetics of a carbon fiber reinforced polyimide (CFRPI) composite to model long-term degradation processes was investigated. The study utilized off-gas analysis to understand degradation behavior and mass-loss curves recorded under dynamic conditions for kinetic interpretations. Four overlapping reaction steps were identified and separated using peak fitting of derivative thermogravimetric curves, accounting for their asymmetrical nature. Each reaction step was analyzed individually using the Friedman method and experimental master-plots. Four kinetic parameters sets were determined to characterize the entire degradation process. Weight loss curves for each reaction at different heating rates, covering the conversion ($\alpha$) range from 0.10 to 0.90, were constructed by integrating and normalizing the fitted differential curves. The Friedman method was then used to calculate activation energies for each reaction. Using these kinetic parameters, long-term aging predictions for the CFRPI composite at 400°C were developed. The predicted weight loss and changes in flexural properties showed strong correlation with experimental results, validating the kinetic model.

In [37], the pyrolysis process of carbon fiber composite cores using TGA experiments conducted at various heating rates was analyzed. Activation energy was calculated using the FWO method due to its ability to determine $E_a$ without assuming a specific reaction mechanism. The Kissinger method was also applied for comparison. Both methods yielded similar results. The study found that $E_a$ remained stable during the early and middle stages of the reaction but increased during the late stages. This increase was attributed to deeper reactions at higher temperatures, requiring more energy to break the physical and chemical cross-links of the epoxy resin molecules. The pyrolysis process was divided into two stages: a stable $E_a$ phase in the early reaction and a gradual increase in $E_a$ in the later stage. The average activation energy for the entire reaction was calculated to be 177.59 kJ/mol. These findings enhance the understanding of the reaction kinetics in carbon fiber composite cores.

The work of [38] focused on the thermal degradation characteristics and kinetics of epoxy resin in CFRPs, with the aim of optimizing recycling via pyrolysis. TG data were analyzed using two isoconversional methods: the Friedman (FR) differential method and the Kissinger–Akahira–Sunose (KAS) integral method. Fluctuations in the activation energies derived from these methods suggested complex reaction mechanisms. To better capture these complexities, the multi-Gaussian distributed

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activation energy model (MG-DAEM) was employed. This model provided a more nuanced understanding of the degradation process of epoxy resin. Key findings include:

Iso-Conversional Analysis: The Friedman method identified three distinct reaction stages within the temperature range of 280–540°C: Stage 1: $\alpha$=5%, $E_a$=158 kJ/mol, Stage 2: At $\alpha$=10-60%, $E_a$=179–190 kJ/mol, and Stage 3: $\alpha$>60%, $E_a$=190–236 kJ/mol.

MG-DAEM Analysis: Thermal decomposition of the epoxy resin was modeled with two Gaussian activation energy distributions, representing the degradation stages: Two Gaussian peaks with similar contributions of 0.58 and 0.42, and activation energy distributions of 217.76 ± 3.92 kJ/mol and 233.36±21.42 kJ/mol, respectively, which are close to the activation energies from iso-conversional analysis at $\alpha$=10-60% and $\alpha$>60%, respectively.

Impact of Carbon Fiber: The presence of carbon fiber significantly influenced the pyrolysis kinetics of epoxy resin. The degree of this influence depended on the mixing methodology applied, affecting the interaction between resin and fibers. These findings demonstrate that MG-DAEM provides a robust framework for characterizing the thermal decomposition of epoxy resin in CFRP composites, improving the understanding of pyrolysis mechanisms and guiding efficient recycling strategies.

#### 4.1.2. Analysis of the Solvolysis process

Like the pyrolysis process, studies in literature have also analyzed the solvolysis process through kinetic methods, primarily based on the Arrhenius equation and simplified reaction models. Following the analytical approach, these studies mainly calculate the degree of depolymerization and the degradation of recyclates. Validation is typically performed by comparing experimental data with theoretical models at specific stages of the process. Typical examples of relevant studies are represented below.

Studies by [24] and [39] highlighted effective resin decomposition techniques enabling the recovery of high-quality carbon fibers (CFs) with minimal mechanical and electrical property loss. In [24] epoxy resin decomposition in CFRP using a 1.5M mCPBA solution at 40°C, achieving complete breakdown in 6 hours was optimized. Depolymerization followed a pseudo-first-order reaction, modeled with a simplified kinetic equation. FT-IR analysis of de-composition products elucidated the mechanism, while energy consumption was calculated for each reaction stage. The recovered CFs retained 93.6% of virgin tensile strength, 95% of electrical conductivity, and a 26% improvement in interfacial shear strength (IFSS) when reused with epoxy resin. Meanwhile, [39] applied thermal hydrolysis in a batch reactor at 523–673 K, using a second-order kinetic model with the Arrhenius equation to describe the process, which involved mass transfer and surface reactions as key steps. Limitations from nonstationary heating phases were noted, but improved mixing efficiency enhanced mass transfer coefficients. Despite minor tensile strength reductions (2–10%), recovered CFs exhibited mechanical properties com-parable to virgin fibers, demonstrating the potential for scalable and efficient CFRP recycling methods.

A subsequent study highlights the utility of reaction-rate-limited models, such as the Arrhenius equation and the shrinking core model (SCM), in effectively predicting the de-composition processes in CFRPs, with experimental data validating the accuracy of these models. [13] investigated the decomposition of CFRPs made with RTM6 resin and T700 carbon fibers in an acetone/water solvent. In this analysis, both a first-order reaction rate equation based on the Arrhenius expression and a reaction-rate-limited SCM were successfully fitted to the experimental data. At all temperatures investigated using the Arrhenius equation, it was observed that there was some mass loss before reaching the specified process conditions. Therefore, it was necessary to model the degradation reaction separately during the heating phase and the reaction phase. In contrast, the SCM assumes that the reaction be-gins at the particle surface, with reactants progressively moving into the particle as time progresses, leaving behind a product or "ash" layer. Among SCM variations, the only model that fits the experimental data was the one for a reaction-rate-limited spherical particle. The results demonstrated that either approach could predict resin decomposition within ±5%, which is within the margin of experimental error.

The last research underscores the significant role of solvents in enhancing resin decomposition rates, with solvent efficacy being closely linked to specific chemical properties like the Hansen solubility parameter. [41] investigated the chemical recycling of CFRPs using supercritical alcohols and ketones as solvents, including supercritical acetone, which emerged as the most effective. The de-composition rate of the epoxy resin in these solvents was expressed using a surface reaction mechanism and SCM, with the resin assumed to be spherically shaped. The Hansen solubility parameter was utilized to estimate the solvency power of the solvents for the decomposition products and to evaluate the relationship between resin decomposition efficiencies and solvent types. Both the surface reaction and SCM effectively described the decomposition rate of the epoxy resin. These findings demonstrated that the decomposition rate was dependent on the type of solvent, with acetone providing optimal performance, thereby highlighting the critical role of solvent selection in enhancing the efficiency of the recycling process.

Many researchers have analyzed the dissolution of thermosetting epoxy in a pure epoxy sample, hypothesizing usually that the carbon fibers have no interaction with the degradation process and are not involved in any chemical reaction. These studies emphasize the critical role of temperature, solvent choice, and catalyst concentration in optimizing solvolysis processes for recycling thermoset composites, while offering insights into future areas of research and application in this field.

The works of [42,43] concentrated on the experimental analysis of solvolysis processes, aiming to identify optimal reaction conditions, such as temperature, pressure, and feedstock ratios, to enhance the decomposition of thermosetting materials. Specifically, [42] explored the impact of experimental parameters to optimize reaction conditions, identifying over twenty types of compounds via HPLC in acetone solvents. The cleavage of cross-linked bonds was assumed to follow a first-order reaction mechanism, and the activation energy for cured epoxy resin decomposition, calculated using rate constants at different temperatures based on the Arrhenius equation, was found to be 123.5 kJ/mol. The study also demonstrated successful epoxy resin decomposition in near-critical water without any additives, with temperature significantly influencing the decomposition percentage and product composition.

Similarly, [44] utilized an industrial-grade epoxy thermoset as a model system to demonstrate efficient thermoset dissolution through alcoholysis under mild conditions. The dissolution kinetics were analyzed using the classical solid-state reaction theory, particularly the contracting cube model, to describe the dissolution process. A theoretical model incorporating alcoholysis kinetics and diffusion behavior was proposed to provide a quantitative under-standing of the dissolution rate. Findings indicated that increasing catalyst concentration enhanced the dissolution rate, correlating closely with the transesterification rate. FTIR analysis further characterized the chemical structure of the recycled products, revealing that alcohols with larger diffusivity and better solubility increased alcohol/catalyst concentrations in the gel layer, thereby accelerating the erosion and dissolution of the epoxy.

[45], similar to the study of [43], examined the role of solvents, their diffusion behavior, and interactions with thermoset materials during the dissolution process. Employing a solvent-assisted dissolution approach, they developed the first multi-scale modeling framework to predict the dissolution kinetics and mechanics of thermosets in organic solvents. This model integrated micro-scale network dynamics with macro-scale material properties. FTIR tests were conducted to track the conversion of ester groups during epoxy dissolution. The dissolution rate was linked to polymer chain diffusivity within both the network and boundary layers. Based on the kinetics of bond exchange reactions (BERs), a micro-scale model was constructed to describe the chain segment length distribution over time, employing Fickian diffusion principles. However, experimental results showed non-Fickian diffusion behavior of alcohol solvent in Covalent Adaptive Networks (CANs) due to the presence of BERs. This model successfully predicted various phenomena, including organic solvent diffusion in CANs, functional group conversions, network modulus evolution, and CAN dis-solution rates, using a single fitting parameter.

Likewise, [46] focused on theoretical and computational approaches to model solvolysis kinetics. They conducted computational studies to elucidate chemical reaction mechanisms and derive kinetic

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and thermodynamic activation parameters. Activation energy (93.37 kJ/mol) and activation free energy were calculated using a combination of Eyring and Arrhenius equations, alongside the enthalpy and entropy of activation determined from Eyring equation plots. The computational predictions aligned closely with experimental results, showing deviations of less than 5%.

A comparison of these studies on solvolysis kinetics reveals a deeper understanding of thermoset dissolution. [42] highlighted temperature's critical role in enhancing decomposition rates, with an activation energy of 123.5 kJ/mol. [45] expanded on this by using multi-scale modeling to emphasize solvent diffusivity and polymer network dynamics' effects on dissolution. [43] showed that catalyst concentration could accelerate dissolution rates, especially in alcoholysis, underlining the impact of reaction conditions. The computational insights from [46] validated these findings by linking theoretical activation parameters with experimental observations, enriching the understanding of solvolysis kinetics.

The following table summarizes the methods of analysis for thermal and chemical degradation processes, providing an overview of the most used approaches for optimizing the recycling process.

**Table 1.** Explanatory table summarizing the methods of analysis for thermal and chemical degradation processes for each study.

| Recycling Method | Author | Method of Analysis |
|---|---|---|
| Pyrolysis | Wang & Zhang, Shen et al. | Kissinger and FWO method |
| | Hadigheh et al. | Friedman, FWO, KAS and Starink methods and Coats-Redfern curve fitting method |
| | Wei & Hadigheh | Friedman and FWO method and Coats-Redfern curve fitting method |
| | Zhang et al. | FWO and KAS method |
| | Cunliffe et al., Chippendale et al. | Arrhenius equation |
| | Xiao et al. | Málek method and different equation forms like FWO, KAS and Starink. |
| | H. Li et al. | Kissinger, Friedman differential method, Ozawa integral method and Coats and Redfern method |
| | Cheng, Sun, et al. | Levenberg–Marquardt method and universal global optimization method |
| | Ren et al. | Density functional theory |
| | Ma et al. | DAEM method and Miura and Maki |
| | Torres-Herrador et al., Y. Liu et al. | Friedman method |
| | K.-W. Kim et al. | Kissinger method |
| Solvolysis | Jeong et al. | Equation of D. H. Kim et al. |
| | Piñero-Hernanz et al. | Arrhenius equation |
| | Keith et al. | Arrhenius expression and SCM method |
| | Y. Y. Liu et al. | Arrhenius equation |
| | Kuang et al. | Classical solid-state reaction theory |
| | Yu et al. | Classic Fickian diffusion |
| | Uliana et al. | Combination of the Eyring and Arrhenius equations |

### *4.2. Computational Insights into CFRP Recycling Techniques*

#### 4.2.1. Simulation of the Pyrolysis process

[47–49] explored the development of models to simulate and predict the pyrolysis process, incorporating various thermodynamic and kinetic parameters. [47] utilized Aspen Plus software to model the upgrading process of pyrolysis vapors and gases, creating equilibrium and kinetic multi-reaction models to forecast the composition of gaseous streams as a function of process parameters such as temperature ($T$), pressure ($P$), and reactor dimensions. The model was validated by comparing its predictions with experimental data, showing good agreement at temperatures of 700°C and 900°C with $\Delta P = 0$ bar. The results revealed that the system preferentially generates lighter chemical compounds under sufficient temperature and time conditions.

[48] applied the ThermaKin2D numerical modeling environment to perform inverse analyses on experimental data, indirectly determining thermo-physical properties and reaction parameters related to the thermal degradation of carbon fiber composite samples. Using a four-reaction mechanism with Arrhenius rate constants, the model successfully represented the thermo-gravimetric and energetic behavior of the composites. The reactions were modeled as first-order, except for the final reaction, which was second-order. This approach allowed the model to closely replicate experimental mass loss and gasification rates, with an aggregate heat of combustion calculated as $2.73\times10^7$ J/kg of volatiles, aligning with literature-reported values of $2.653\times10^7$ J/kg. Uncertainty analysis was conducted by independently varying kinetic parameters while maintaining the error within the experimental data's mean scatter, further validating the model's robustness.

These models highlight the potential of predictive simulations in optimizing pyrolysis processes for recycling carbon fiber composites and other materials.

In [49], the Fire FOAM CFD solver to model the one-dimensional pyrolysis of condensed phases in two carbon-reinforced composites: a thermosetting phenolic resin and a thermoplastic PEKK was utilized. A sensitivity analysis evaluated the model's response to variations in parameters. Kinetic parameters for resin decomposition, oxidation of char, and fiber consumption were derived from TGA-based mass loss data under inert and oxidative conditions. Using Friedman’s iso-conversional methods, values for $E_a$, pre-exponential factor $A$, and reaction order $n$ were calculated across temperature intervals defined by TG measurements. Numerical simulations aligned closely with experimental results, maintaining a quasi-constant value until 30 seconds, followed by a mass decrease, culminating in a final mass loss of 13%. After 170 seconds, decomposition behavior differences emerged, particularly for carbon PEKK, indicating sensitivity in activation energy during fiber decomposition. The study emphasizes the impact of material density and activation energy on mass loss rates and temperature profiles, underscoring the distinct pyrolysis behaviors of the two composites.

In [11,50] optimizing the pyrolysis process by simulating various conditions and validating findings with experimental data was explored. [32] established a representative volume element (RVE) for CFRPs to study structural damage during recycling using Digimat's thermomechanical coupling module, analyzing stress and strain distributions. CFRPs were decomposed into carbon fibers by heating powdered $Cr_2O_3$ to 500°C, achieving an epoxy resin removal rate above 90%. Stress and strain distribution, including thermal, shear, and peeling stresses, were calculated using the enhanced Reddy theory. Thermal stress, shear stress, and peeling stress increased with temperature, identifying potential damage regions in the epoxy resin and interface layers. Damage mechanisms included microcrack formation leading to interfacial debonding and delamination caused by excessive peeling stress in the resin matrix. Meanwhile, [50] developed a mathematical prediction model for determining optimal parameters for thermal recycling of TS-CFRP composites using MATLAB-based finite difference methods. The model calculated furnace heating rates within specified limits and validated sub-models for heat transfer, material conversion, and radiation view factor with experimental data. Results showed less than ±2% variance in matrix mass loss behavior at peak degradation rates and consistency with TGA results up to 800°C. The model reliably predicted furnace process parameters and layer-wise matrix mass loss distribution, with an error margin of five percent, though improvements could further refine multistage degradation modeling.

[51] conducted a comprehensive testing campaign to examine the pyrolysis rate of various CFRPs under re-entry heating conditions and its impact on their ultimate strength, focusing on

CFRPs with epoxy, cyanate ester, vinyl ester, and phenolic resins. The hot wall heat flux was calculated from the surface temperature of the sample, while the cold wall heat flux was measured pre-test. TGA data were processed using MATLAB with piecewise functions applied for efficient curve analysis. A new time-accurate finite difference code was developed to simulate the char depth test, leveraging material properties and recently developed TGA mass fraction models. Model accuracy was validated by comparing measured and simulated front- and back-surface temperature profiles. Additionally, a novel thermal charring model, developed using TGA data, was validated against char depth rate tests, showing strong agreement with experimental data for char depth and surface temperature profiles across the tested materials.

### 4.2.2. Simulation of the Solvolysis process

The screening of the recycling process can be effectively conducted using specialized simulation software. This approach is based on the previous analytical models, and the simulation results are then validated by comparing them to experimental data. More specifically, solvolysis and pyrolysis processes are typically analyzed through simulations that model the dissolution of the thermosetting matrix.

[52,53] utilized Finite Element Analysis (FEA) models to explore solvolysis and depolymerization in CFRPs by linking microscale bond-exchange kinetics to continuum-level composite behaviors. [52] developed a diffusion-reaction-mechanics FEA computational model to predict matrix curing degree, residual stress around fibers, and mechanical properties, aligning with experimental findings. Parametric studies assessed the effects of temperature, fiber content, solvent diffusivity, and bond-exchange reactions (BERs) to optimize recycling efficiency and minimize residual stress. Carbon fibers, modeled as rigid solids due to their high modulus and solvent inertness, were integrated into a MATLAB-based custom finite element code employing 2D triangular elements to solve diffusion partial differential equations. Close to the previous study, [54] constructed a multiscale diffusion-reaction computational model based on FEM to link BER rates to composite depolymerization kinetics. The model explored how processing conditions, such as temperature, solvent diffusivity, fiber content, and arrangement, affect depolymerization rates. Depolymerization tests on thin-film lamina samples treated the process as a 2D plane strain diffusion-reaction problem. The study revealed that increasing temperature or solvent diffusivity enhances the depolymerization rate, providing close predictions of swelling and matrix depolymerization behaviors under varying material and processing conditions.

[55] also utilized finite element analysis (FEA) but focused on simulating phase transitions and solvent diffusion as localized phenomena influenced by the degree of polymerization. Using a phenomenological approach, the dissolution of an epoxy matrix was modeled as a local phase transition affected by temperature, solvent diffusion, and microstructural factors. Implemented in the finite element code Abaqus with user-defined field and heat flux subroutines, the model accounted for an increasing diffusion coefficient with the degree of polymerization and the influence of composite porosity. The simulation aligned well with experimental results for the first 180 minutes, during which the composite's cross-section shrank as solvent penetrated the epoxy matrix. Over time, the simulated sample exhibited a smaller, rounder shape, likely due to the absence of swelling effects and excessive solvent concentration evolution at the corners.

[56,57] employed chemical and diffusion-based simulation models to investigate the concentration of chemical species and diffusion during the dissolution of carbon fiber/epoxy composites, focusing on the impact of temperature and solvent conditions on material proper-ties such as stress and strain during solvolysis. [56] developed a reaction-diffusion coupling framework to study how reinforcement affects the dissolution process of CFRPs. Using a chemical species concentration-dependent model, they analyzed the evolution of functional group concentrations and network structures via solvent-assisted exchange reactions. The equations were solved in COMSOL Multiphysics using the finite element method (FEM) on a cubic domain that matched experimental pure resin samples. This model, extended to thermosetting polymers and composites without embedded catalysts, showed reasonable agreement with experimental results upon calibration and

enabled parametric studies on carbon fiber mass fraction, reducing the need for extensive experimental work. [57] utilized ANSYS software to analyze the stress and strain distributions of carbon fiber/epoxy resin laminates decomposed under varying temperatures and pressures in near-critical water. They examined five-layer laminates and compared them to laminates with different numbers of layers. Results indicated that increasing the number of layers heightened interlaminar shear stress, peeling stress, and displacements in the y direction while decreasing displacements in the x direction

[58] developed a solvent screening method that utilizes theoretical descriptors derived from COSMO-RS quantum chemical computations and advanced statistical techniques to quantify solvent effects on chemical reactions. The COSMO-RS methodology involves two main steps: quantum chemical computation and statistical thermodynamics treatment. This approach was applied to assess solvent effects on the reaction rate for two nucleophilic substitution reactions and the reaction selectivity for one Diels–Alder reaction, with models built by correlating experimental reaction properties in various solvents with their molecular descriptors. New solvent data were obtained via standard DFT calculations, enabling efficient prescreening of solvents in the early stages of chemical process design. In contrast, [59] focused on quantifying cradle-to-gate (C2G) energy intensities, environmental impacts, and human health burdens associated with producing one functional unit of 17 candidate supercritical fluids (SCFs) proposed for depolymerizing thermoset resins in CFRP waste. Using Aspen HYSYS, 17 simulation cases were developed to calculate energy requirements and mid-point impact categories for SCF production under varying temperature and pressure conditions. The study highlighted that increasing reaction temperature and pressure to improve resin removal efficiency incurs a significant energy penalty during SCF production.

In addition, a summarized table is presented below, recording the simulation software which is used for each author.

**Table 2.** Summarized table recording the simulation software which each author utilized.

| Recycling Method | Author | Simulation Software |
|---|---|---|
| Pyrolysis | Serras-Malillos et al. | Aspen Plus |
| | McKinnon et al. | ThermaKin2D |
| | Grange et al. | Fire FOAM CFD solver |
| | Cheng, Chang, et al. | Digimat |
| | Qazi et al., Greene & Ostrom | Finite difference methods in MATLAB |
| Solvolysis | Chung et al., Luo et al. | FEA model in MATLAB |
| | Chen & Mishnaevsky | Finite element code Abaqus |
| | Hamel et al. | FEA model in COMSOL |
| | Jia et al. | ANSYS |
| | Zhou et al. | COSMO-RS |
| | Khalil | Aspen HYSYS |

### *4.3. Analysis of Pyrolysis process of CFRPs in combination with other phenomena*

During the solvolysis and pyrolysis processes, other mechanisms can be activated, such as the initiation of cracks. In addition, the process of thermal degradation developed in chemical and thermal recycling in CFRPs can also model other phenomena, including lightning strikes.

[60] investigated the pyrolysis process in CFRPs, focusing on the thermal decomposition of the polymeric matrix into amorphous carbon and the resulting crack patterns to tailor composites based on process parameters. The study modeled material behavior during pyrolysis, considering thermal effects but not differentiating between thermal and chemical contributions to expansion. Assumptions included a homogeneous matrix, linear elastic behavior, and constant material properties across temperatures. While the model effectively reproduced behavior for weak fiber/matrix strength, it predicted microcracks in the matrix for strong fiber/matrix strength that were not confirmed by SEM images. Similarly, [61] developed a pyrolysis-dependent model to study lightning strike damage in composite laminates. The model utilized pyrolysis kinetic equations

derived from TGA and incorporated Scheil's superposition principle, typically used for non-isothermal phase changes, to calculate the impact of pyrolysis during lightning strikes. The model closely matched experimental observations of in-depth damage but tended to underestimate in-plane damage, whereas temperature-dependent models overestimated in-depth damage.

## 4. Discussion

In summary, these studies explored present the significant perspective of solvolysis and pyrolysis as promising recycling methods for CFRPs. Each of these studies offers valuable insights into different process parameters, such as temperature, pressure and solvent choice, with respect to their impact on the efficiency of CFRP recycling. While solvolysis provides milder reaction conditions and potential solvent reuse, pyrolysis provides a more direct approach for the depolymerization of composite matrices into valuable by-products. These methods show promising results in terms of fiber recovery and matrix decomposition, but there are still some drawbacks in optimizing the efficiency of these processes for industrial-scale applications.

In the case of pyrolysis, various methods for the recycling and degradation of CFRPs are highlighted, focusing on thermal decomposition, oxidation and supercritical fluid treatments. Most common approaches like TGA were employed to investigate the multi-stage degradation of both the polymer matrix and carbon fibers. Methods like Friedman, KAS, and Coats-Redfern for kinetic analysis were used. The oxidation and the use of supercritical fluids demonstrated potential for valuable fiber recovery and minimum damage. Additionally, techniques like density functional theory and the multi-Gaussian distributed activation energy model provided deeper insights into the activation energies and reaction mechanisms involved.

Kinetic analysis of solvolysis in CFRPs typically employs the Arrhenius equation and SCM to model resin decomposition. Studies have proved that the depolymerization of epoxy resin follows a pseudo-first-order reaction, with a constant reaction rate. For example, both the Arrhenius equation and SCM have been successfully used to model decomposition with solvents like acetone and mCPBA, showing strong connection with experimental data. Additionally, energy consumption during the solvolysis process has been a critical topic of recent studies, with several researchers calculating the energy required for each reaction stage to optimize the efficiency of carbon fiber recovery and resin decomposition in recycling processes.

Simulation techniques studied the solvolysis process in CFRPs, with a focus on modeling composite behavior during dissolution and depolymerization. Finite element analysis was mostly used to assess how factors such as temperature, solvent diffusivity, and fiber content affect material properties, such as curing degree and stress development. Additionally, chemical and diffusion-based models explored dissolution kinetics and solvent interactions. These computational approaches enhance optimizing recycling conditions and minimizing environmental impact. This review also focuses on simulating the pyrolysis of CFRPs, emphasizing thermal degradation processes such as resin dissolution and oxidation. Unlike solvolysis, which centers on chemical dissolution, pyrolysis models focus on temperature and pressure effects on mass loss and structural damage like delamination. Various simulation tools are used, including Aspen Plus for kinetic and equilibrium models, ThermaKin2D for thermophysical property analysis, and Fire FOAM CFD for modeling pyrolysis under varying conditions. While both pyrolysis and solvolysis rely on similar computational approaches, pyrolysis primarily addresses thermal processes, whereas solvolysis focuses on solvent-driven chemical reactions.

The selection of modelling techniques for pyrolysis and solvolysis processes in CFRPs depends on the specific objectives of the analysis. For pyrolysis, Arrhenius-based models are sufficient for simple systems, whereas Coats-Redfern models provide better accuracy for multi-stage reactions. Detailed results can be achieved using COMSOL for reaction-diffusion coupling, which captures chemical and physical interactions effectively, though it requires significant computational resources. In solvolysis, FEA models are effective for capturing stress and diffusion effects, while reaction-diffusion models, such as those implemented in MATLAB, offer a balance between computational efficiency and predictive accuracy. COSMO-RS enables rapid solvent screening for early-stage process optimization. Combining multiple techniques can provide a practical balance between accuracy and computational efficiency.

Overall, this review paper highlights the potential for developing more efficient and sustainable recycling methods for CFRPs, which is a critical subject because the challenges related to composite material waste are increasing day by day. By improving and using these models, industry can make big progress in creating more efficient recycling processes which reduce the environmental impact.

Future research should aim to optimize solvolysis and pyrolysis processes for more efficient CFRP recycling. Specifically, exploring the development of more sustainable and cost-effective solvents for solvolysis, as well as improving reaction kinetics and energy efficiency in pyrolysis, could significantly improve the overall recycling process. Finally, further research on reusing recovered fibers and incorporating recycled CFRPs into new structures could pave the way for closed loop recycling systems, contributing to the circular economy.

**Supplementary Materials:** The following supporting information can be downloaded at: Preprints.org.

**Author Contributions:** Conceptualization, I.T. and K.T.; methodology, I.T. and K.T.; investigation, I.T. and K.T.; re-sources, I.T.; data curation, I.T.; writing—original draft preparation, I.T.; writing—review and editing, I.T. and K.T.; visualization, I.T.; supervision, K.T.; project administration, K.T.; funding acquisition, K.T. All authors have read and agreed to the published version of the manuscript.

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## References

1. Xiao, P.; Zhang, J.; Li, H.; Mou, H.; Feng, Z.; Xie, J. Pyrolysis Kinetics Analysis and Prediction for Carbon Fiber-Reinforced Epoxy Composites. *Polymers* **2023**, *15*, 4533. https://doi.org/10.3390/polym15234533.
2. Oliveux, G.; Dandy, L.O.; Leeke, G.A. Current Status of Recycling of Fibre Reinforced Polymers: Review of Technologies, Reuse and Resulting Properties. *Prog. Mater. Sci.* **2015**, *72*, 61–99. https://doi.org/10.1016/j.pmatsci.2015.01.004.
3. Guirdham, O. Carbon Fiber Reinforced Plastic (CFRP) Global Market 2024 To Reach $20.19 Billion By 2028 At Rate Of 10.1% Available online: https://www.einpresswire.com/article/754460158/carbon-fiber-reinforced-plastic-cfrp-global-market-2024-to-reach-20-19-billion-by-2028-at-rate-of-10-1 (accessed on 14 November 2024).
4. Pei, C.; Chen, P.; Kong, S.-C.; Wu, J.; Zhu, J.-H.; Xing, F. Recyclable Separation and Recovery of Carbon Fibers from CFRP Composites: Optimization and Mechanism. *Sep. Purif. Technol.* **2021**, *278*, 119591. https://doi.org/10.1016/j.seppur.2021.119591.
5. Li, J.; Xu, P.-L.; Zhu, Y.-K.; Ding, J.-P.; Xue, L.-X.; Wang, Y.-Z. A Promising Strategy for Chemical Recycling of Carbon Fiber/Thermoset Composites: Self-Accelerating Decomposition in a Mild Oxidative System. *Green Chem.* **2012**, *14*, 3260. https://doi.org/10.1039/c2gc36294e.
6. Liu, Y.; Liu, J.; Jiang, Z.; Tang, T. Chemical Recycling of Carbon Fibre Reinforced Epoxy Resin Composites in Subcritical Water: Synergistic Effect of Phenol and KOH on the Decomposition Efficiency. *Polym. Degrad. Stab.* **2012**, *97*, 214–220. https://doi.org/10.1016/j.polymdegradstab.2011.12.028.
7. Li, H.; Englund, K. Recycling of Carbon Fiber-Reinforced Thermoplastic Composite Wastes from the Aerospace Industry. *J. Compos. Mater.* **2017**, *51*, 1265–1273. https://doi.org/10.1177/0021998316671796.
8. Utekar, S.; V K, S.; More, N.; Rao, A. Comprehensive Study of Recycling of Thermosetting Polymer Composites – Driving Force, Challenges and Methods. *Compos. Part B Eng.* **2021**, *207*, 108596. https://doi.org/10.1016/j.compositesb.2020.108596.
9. Tranchard, P.; Duquesne, S.; Samyn, F.; Estèbe, B.; Bourbigot, S. Kinetic Analysis of the Thermal Decomposition of a Carbon Fibre-Reinforced Epoxy Resin Laminate. *J. Anal. Appl. Pyrolysis* **2017**, *126*, 14–21. https://doi.org/10.1016/j.jaap.2017.07.002.
10. Wei, Y.; Hadigheh, S.A. Enhancing Carbon Fibre Recovery through Optimised Thermal Recycling: Kinetic Analysis and Operational Parameter Investigation. *Mater. Today Sustain.* **2024**, *25*, 100661. https://doi.org/10.1016/j.mtsust.2023.100661.
11. Cheng, H.; Sun, Y.; Zhou, Z.; Zhang, J.; Wang, X.; Chang, J. Kinetics of Recycling CF/EP Composites by Thermal Excitation of Cr2O3. *J. Polym. Environ.* **2019**, *27*, 1937–1947. https://doi.org/10.1007/s10924-019-01482-3.

12. Liu, Y.; Xu, X.-Z.; Mo, S.; Lan, B.-W.; Zhu, C.-Z.; Li, C.-H.; Xu, J.; Fan, L. Long-Term Thermo-Oxidative Degradation Modeling of a Carbon Fiber Reinforced Polyimide Composite: Multistep Degradation Behaviors and Kinetics. *Chin. J. Polym. Sci.* **2020**, *38*, 1202–1213. https://doi.org/10.1007/s10118-020-2425-7.
13. Keith, M.J.; Román-Ramírez, L.A.; Leeke, G.; Ingram, A. Recycling a Carbon Fibre Reinforced Polymer with a Supercritical Acetone/Water Solvent Mixture: Comprehensive Analysis of Reaction Kinetics. *Polym. Degrad. Stab.* **2019**, *161*, 225–234. https://doi.org/10.1016/j.polymdegradstab.2019.01.015.
14. Mortezaeikia, V.; Tavakoli, O.; Khodaparasti, M.S. A Review on Kinetic Study Approach for Pyrolysis of Plastic Wastes Using Thermogravimetric Analysis. *J. Anal. Appl. Pyrolysis* **2021**, *160*, 105340. https://doi.org/10.1016/j.jaap.2021.105340.
15. Lee, J.H.; Kim, K.S.; Kim, H. Determination of Kinetic Parameters during the Thermal Decomposition of Epoxy/Carbon Fiber Composite Material. *Korean J. Chem. Eng.* **2013**, *30*, 955–962. https://doi.org/10.1007/s11814-012-0224-8.
16. Li, H.; Wang, N.; Han, X.; Yuan, H.; Xie, J. Mechanism Identification and Kinetics Analysis of Thermal Degradation for Carbon Fiber/Epoxy Resin. *Polymers* **2021**, *13*, 569. https://doi.org/10.3390/polym13040569.
17. Horowitz, H.H.; Metzger, Gershon. A New Analysis of Thermogravimetric Traces. *Anal. Chem.* **1963**, *35*, 1464–1468. https://doi.org/10.1021/ac60203a013.
18. Avrami, M. Kinetics of Phase Change. I General Theory. *J. Chem. Phys.* **1939**, *7*, 1103–1112. https://doi.org/10.1063/1.1750380.
19. Hadigheh, S.A.; Wei, Y.; Kashi, S. Optimisation of CFRP Composite Recycling Process Based on Energy Consumption, Kinetic Behaviour and Thermal Degradation Mechanism of Recycled Carbon Fibre. *J. Clean. Prod.* **2021**, *292*, 125994. https://doi.org/10.1016/j.jclepro.2021.125994.
20. Starink, M.J. A New Method for the Derivation of Activation Energies from Experiments Performed at Constant Heating Rate. *Thermochim. Acta* **1996**, *288*, 97–104. https://doi.org/10.1016/S0040-6031(96)03053-5.
21. Ma, C.; Sánchez-Rodríguez, D.; Kamo, T. A Comprehensive Study on the Oxidative Pyrolysis of Epoxy Resin from Fiber/Epoxy Composites: Product Characteristics and Kinetics. *J. Hazard. Mater.* **2021**, *412*, 125329. https://doi.org/10.1016/j.jhazmat.2021.125329.
22. Schamel, E.; Wehnert, G.; Schlachter, H.; Söthje, D. Chemical Recycling of Carbon Fiber Reinforced Epoxy Composites Using Mild Conditions. *Chem. Ing. Tech.* **2021**, *93*, 1619–1628. https://doi.org/10.1002/cite.202100048.
23. Zhang, X.; Hu, A.; Pan, C.; Zhao, Q.; Wang, X.; Lu, J. Safer Preparation of *m*- CPBA/DMF Solution in Pilot Plant. *Org. Process Res. Dev.* **2013**, *17*, 1591–1596. https://doi.org/10.1021/op400208b.
24. Jeong, J.; Oh, D.; Ju, Y.; Goh, M. Energy-Efficient Chemical Recycling of CFRP and Analysis of the Interfacial Shear Strength on Recovered Carbon Fiber. *Waste Manag.* **2024**, *187*, 134–144. https://doi.org/10.1016/j.wasman.2024.07.017.
25. Kim, K.-W.; Jeong, J.-S.; An, K.-H.; Kim, B.-J. A Low Energy Recycling Technique of Carbon Fibers-Reinforced Epoxy Matrix Composites. *Ind. Eng. Chem. Res.* **2019**, *58*, 618–624. https://doi.org/10.1021/acs.iecr.8b02554.
26. Wang, H.; Zhang, L. Pyrolysis and Combustion Characteristics and Reaction Kinetics of Carbon Fiber/Epoxy Composites. *AIP Adv.* **2019**, *9*, 125110. https://doi.org/10.1063/1.5128460.
27. Wei, Y.; Hadigheh, S.A. Optimising CFRP Recycling via Arrhenius-Type Kinetic Behaviour Analysis. In *10th International Conference on FRP Composites in Civil Engineering*; Ilki, A., Ispir, M., Inci, P., Eds.; Lecture Notes in Civil Engineering; Springer International Publishing: Cham, 2022; Vol. 198, pp. 1110–1118 ISBN 978-3-030-88165-8.
28. Zhang, Z.; Wang, C.; Huang, G.; Liu, H.; Yang, S.; Zhang, A. Thermal Degradation Behaviors and Reaction Mechanism of Carbon Fibre-Epoxy Composite from Hydrogen Tank by TG-FTIR. *J. Hazard. Mater.* **2018**, *357*, 73–80. https://doi.org/10.1016/j.jhazmat.2018.05.057.
29. Cunliffe, A.M.; Jones, N.; Williams, P.T. Recycling of FIbre-Reinforced Polymeric Waste by Pyrolysis: Thermo-Gravimetric and Bench-Scale Investigations.
30. Chippendale, R.D.; Golosnoy, I.O.; Lewin, P.L. Numerical Modelling of Thermal Decomposition Processes and Associated Damage in Carbon Fibre Composites. *J. Phys. Appl. Phys.* **2014**, *47*, 385301. https://doi.org/10.1088/0022-3727/47/38/385301.
31. Cheng, H.; Huang, H.; Liu, Z.; Zhang, J. Reaction Kinetics of CFRP Degradation in Supercritical Fluids. *J. Polym. Environ.* **2018**, *26*, 2153–2165. https://doi.org/10.1007/s10924-017-1114-2.
32. Cheng, H.; Chang, J.; Sun, Y.; Zhang, J.; Wang, X. Numerical Simulation of Stress Distribution for CF/EP Composites in High Temperatures. *J. Therm. Stress.* **2019**, *42*, 416–425. https://doi.org/10.1080/01495739.2018.1469102.
33. Ren, Y.; Xu, L.; Sun, Y.; Li, X.; Shen, Z.; Li, H.; Liu, J. Study on Oxidation Behavior during Process of Recycling Carbon Fibers from CFRP by Pyrolysis. *J. Environ. Manage.* **2023**, *347*, 119103. https://doi.org/10.1016/j.jenvman.2023.119103.

34. Branca, C.; Di Blasi, C.; Galgano, A.; Milella, E. Thermal and Kinetic Characterization of a Toughened Epoxy Resin Reinforced with Carbon Fibers. *Thermochim. Acta* **2011**, *517*, 53–62. https://doi.org/10.1016/j.tca.2011.01.034.
35. Torres-Herrador, F.; Eschenbacher, A.; Blondeau, J.; Magin, T.E.; Geem, K.M.V. Study of the Degradation of Epoxy Resins Used in Spacecraft Components by Thermogravimetry and Fast Pyrolysis. *J. Anal. Appl. Pyrolysis* **2022**, *161*, 105397. https://doi.org/10.1016/j.jaap.2021.105397.
36. Ge, L.; Li, X.; Feng, H.; Xu, C.; Lu, Y.; Chen, B.; Li, D.; Xu, C. Analysis of the Pyrolysis Process, Kinetics and Products of the Base Components of Waste Wind Turbine Blades (Epoxy Resin and Carbon Fiber). *J. Anal. Appl. Pyrolysis* **2023**, *170*, 105919. https://doi.org/10.1016/j.jaap.2023.105919.
37. Shen, C.; Yin, F.; Wang, L.; Li, R.; Liao, Y.; Gong, B. Thermogravimetric Analysis and Activation Energy Calculation of Carbon Fiber Composite Cores. In Proceedings of the 2020 IEEE International Conference on High Voltage Engineering and Application (ICHVE); IEEE: Beijing, China, September 6 2020; pp. 1–4.
38. Zeng, Y.; Xue, Y.; Gong, X.; Gao, X.; E, J.; Chen, J.; Leng, E. Pyrolytic Performance and Kinetics Study of Epoxy Resin in Carbon Fiber Reinforced Composites: Synergistic Effects of Epoxy Resin and Carbon Fiber. *J. Anal. Appl. Pyrolysis* **2023**, *176*, 106255. https://doi.org/10.1016/j.jaap.2023.106255.
39. Piñero-Hernanz, R.; Dodds, C.; Hyde, J.; García-Serna, J.; Poliakoff, M.; Lester, E.; Cocero, M.J.; Kingman, S.; Pickering, S.; Wong, K.H. Chemical Recycling of Carbon Fibre Reinforced Composites in Nearcritical and Supercritical Water. *Compos. Part Appl. Sci. Manuf.* **2008**, *39*, 454–461. https://doi.org/10.1016/j.compositesa.2008.01.001.
40. Kim, D.H.; Yu, A.; Goh, M. Oxidative Chemical Depolymerization of Thermoset Epoxy Resin for Green Recycling. *J. Ind. Eng. Chem.* **2021**, *96*, 76–81. https://doi.org/10.1016/j.jiec.2021.01.047.
41. Okajima, I.; Watanabe, K.; Haramiishi, S.; Nakamura, M.; Shimamura, Y.; Sako, T. Recycling of Carbon Fiber Reinforced Plastic Containing Amine-Cured Epoxy Resin Using Supercritical and Subcritical Fluids. *J. Supercrit. Fluids* **2017**, *119*, 44–51. https://doi.org/10.1016/j.supflu.2016.08.015.
42. Liu, Y.Y.; Wei, H.; Wu, S.; Guo, Z. Kinetic Study of Epoxy Resin Decomposition in Near-Critical Water. *Chem. Eng. Technol.* **2012**, *35*, 713–719. https://doi.org/10.1002/ceat.201100494.
43. Kuang, X.; Shi, Q.; Zhou, Y.; Zhao, Z.; Wang, T.; Qi, H.J. Dissolution of Epoxy Thermosets *via* Mild Alcoholysis: The Mechanism and Kinetics Study. *RSC Adv.* **2018**, *8*, 1493–1502. https://doi.org/10.1039/C7RA12787A.
44. Kuang, X.; Zhou, Y.; Shi, Q.; Wang, T.; Qi, H.J. Recycling of Epoxy Thermoset and Composites via Good Solvent Assisted and Small Molecules Participated Exchange Reactions. *ACS Sustain. Chem. Eng.* **2018**, *6*, 9189–9197. https://doi.org/10.1021/acssuschemeng.8b01538.
45. Yu, K.; Yang, H.; Dao, B.H.; Shi, Q.; Yakacki, C.M. Dissolution of Covalent Adaptable Network Polymers in Organic Solvent. *J. Mech. Phys. Solids* **2017**, *109*, 78–94. https://doi.org/10.1016/j.jmps.2017.08.006.
46. Uliana, F.; Ambrozio, S.R.; Filho, E.A.S.; Gonçalves, A.S.; Melo, C.V.P.; Luz, P.P.; Silva, C.V.G. Kinetic Study of Depolymerization of Polyurethanes: A Experimental and Computational Insight for Chemical Recycling. *Int. J. Chem. Kinet.* **2020**, *52*, 611–619. https://doi.org/10.1002/kin.21374.
47. Serras-Malillos, A.; Acha, E.; Lopez-Urionabarrenechea, A.; Perez-Martinez, B.B.; Caballero, B.M. Composite Waste Recycling: Predictive Simulation of the Pyrolysis Vapours and Gases Upgrading Process in Aspen Plus. *Chemosphere* **2022**, *300*, 134499. https://doi.org/10.1016/j.chemosphere.2022.134499.
48. McKinnon, M.B.; Ding, Y.; Stoliarov, S.I.; Crowley, S.; Lyon, R.E. Pyrolysis Model for a Carbon Fiber/Epoxy Structural Aerospace Composite. *J. Fire Sci.* **2017**, *35*, 36–61. https://doi.org/10.1177/0734904116679422.
49. Grange, N.; Chetehouna, K.; Gascoin, N.; Coppalle, A.; Reynaud, I.; Senave, S. One-Dimensional Pyrolysis of Carbon Based Composite Materials Using FireFOAM. *Fire Saf. J.* **2018**, *97*, 66–75. https://doi.org/10.1016/j.firesaf.2018.03.002.
50. Qazi, H.; Subiantoro, A.; Lin, R.; Jayaraman, K. Prediction Model of Optimised Process Parameters for Recycling Carbon Fibre Composites. *Therm. Sci. Eng. Prog.* **2022**, *33*, 101344. https://doi.org/10.1016/j.tsep.2022.101344.
51. Greene, B.R.; Ostrom, C.L. PYROLYSIS RATE AND YIELD STRENGTH REDUCTION IN CARBON FIBER AND GLASS FIBER COMPOSITES UNDER REENTRY HEATING CONDITIONS.
52. Chung, C.; Jiang, H.; Luo, C.; Yu, K. Matrix Curing and Stress Field Development around Fiber during the Solvent Evaporation-Induced Repolymerization of Recycling Composites. *Mater. Today Sustain.* **2024**, *26*, 100792. https://doi.org/10.1016/j.mtsust.2024.100792.
53. Luo, C.; Chung, C.; Yu, K. A Diffusion-Reaction Computational Study to Reveal the Depolymerization Mechanisms of Epoxy Composites for Recycling. *Mater. Today Sustain.* **2023**, *23*, 100452. https://doi.org/10.1016/j.mtsust.2023.100452.
54. Luo, C.; Chung, C.; Yu, K. A Diffusion-Reaction Computational Study to Reveal the Depolymerization Mechanisms of Epoxy Composites for Recycling. *Mater. Today Sustain.* **2023**, *23*, 100452. https://doi.org/10.1016/j.mtsust.2023.100452.
55. Chen, Y.; Mishnaevsky, L. Modeling the Solvolysis of Composite Materials of Wind Turbine Blades. *Adv. Eng. Mater.* **2024**, *26*, 2302150. https://doi.org/10.1002/adem.202302150.

56. Hamel, C.M.; Kuang, X.; Qi, H.J. Modeling the Dissolution of Thermosetting Polymers and Composites via Solvent Assisted Exchange Reactions. *Compos. Part B Eng.* **2020**, *200*, 108363. https://doi.org/10.1016/j.compositesb.2020.108363.
57. Jia, X.; Liu, Y.; Li, L. Analysis of Mechanical Properties of Carbon/Epoxy Composites in the near Critical Water Decomposition. *Polym. Polym. Compos.* **2013**, *21*, 573–580. https://doi.org/10.1177/096739111302100904.
58. Zhou, T.; Qi, Z.; Sundmacher, K. Model-Based Method for the Screening of Solvents for Chemical Reactions. *Chem. Eng. Sci.* **2014**, *115*, 177–185. https://doi.org/10.1016/j.ces.2013.11.020.
59. Khalil, Y.F. Sustainability Assessment of Solvolysis Using Supercritical Fluids for Carbon Fiber Reinforced Polymers Waste Management. *Sustain. Prod. Consum.* **2019**, *17*, 74–84. https://doi.org/10.1016/j.spc.2018.09.009.
60. Jain, N.; Kosin, M.; Shi, Y.; Koch, D. Characterization and Modeling of Transverse Micro-cracking during Pyrolysis Process of Carbon Fiber Reinforced Plastics. *Int. J. Appl. Ceram. Technol.* **2019**, *16*, 1734–1743. https://doi.org/10.1111/ijac.13312.
61. Guo, Y.; Dong, Q.; Chen, J.; Yao, X.; Yi, X.; Jia, Y. Comparison between Temperature and Pyrolysis Dependent Models to Evaluate the Lightning Strike Damage of Carbon Fiber Composite Laminates. *Compos. Part Appl. Sci. Manuf.* **2017**, *97*, 10–18. https://doi.org/10.1016/j.compositesa.2017.02.022.

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