

An Investigation on the Thermal Degradation Kinetics of Wood-Polymer Composites Used in Interior Automobile Panels via Non-Isothermal Thermogravimetry

Gamzenur Özsin 

Chemical Engineering Department, Faculty of Engineering, Bilecik Şeyh Edebali University, Bilecik, 11100, Türkiye

Abstract

Wood plastic composites (WPCs) offer a promising alternative for various automotive components, combining the benefits of wood and polymers such as lightness, strength, and sustainability. However, determining decomposition kinetics is challenging due to the intricate composition of WPCs. Therefore, this research work focused to analyze the relationship between the thermal degradation of WPCs, the degradation atmosphere, and the kinetics. The kinetic parameters were evaluated by Coats and Redfern method based on a set of TGA experiments under variable atmospheres (inert and oxidative) using 10 °C/min heating rate. Thermograms demonstrated significant differences in the thermal properties of WPC when subjected to oxidative and inert atmospheres, despite two conditions having the same number of thermal degradation zones. It has been suggested that the process of thermal decomposition of WPC contains three weight loss segments under inert and oxidative atmosphere according to the Gaussian multi-peak fitting function. The Coats-Redfern method showed multi-step chemical kinetics and more accurately characterizes the decomposition behavior of WPC, attributing to its multi-compositional properties. Proposed reaction schemes had regression coefficients higher than 0.9809 to obtain reaction order, activation energy and pre-exponential factor.

Keywords: Coats and Redfern; Decomposition; Kinetics; Thermal behavior; Wood-plastic composite

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Contact

* Corresponding author

Gamzenur Özsin

gamzenur.ozsin@bilecik.edu.tr

Address: Chemical Engineering Department, Faculty of Engineering, Bilecik Şeyh Edebali University, Bilecik, Türkiye
Tel: +902282141534

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1. Introduction

The unprecedented transformation of the automotive sector necessitates an additional cohort of industry-focused researchers to implement and commercialize new technologies, primary product design and manufacturing innovations, and early involvement for low-cost, environmentally friendly materials for the target applications of the vehicles. There is a growing need for lightweight functional composite materials in the automotive industry, driven by the increasing demand to decrease fuel consumption and electrification of the transportation. Moreover, durability, cost and sustainability are the main factors that should be considered during the selection of the proper composites that might be used in the interior and exterior parts of the automobiles [1,2].

Natural fillers of lignocellulosic biomass have numerous advantages over synthetic fillers in the composite structures, in particular for the polymer matrix composites, due to their

biodegradability, low density, and being less abrasive to processing equipment in addition to their superior overall performance [3]. Therefore, incorporation of naturally grown, low-cost lignocellulosic materials inside polymeric matrix is an exciting approach to improving the performance of sustainable materials while ensuring significant economic and environmental sustainability.

Wood-polymer composites (WPCs) are the prosperous materials in automobile industry since manufacturers can benefit from their lightweight nature, sustainability, design flexibility, vibration damping, corrosion resistance, insulation properties, and end-of-life considerations by incorporating wood polymer composites in the automobile industry. Automobile manufacturers such as Mercedes-Benz, Audi, Toyota, and Ford have significantly contributed to decreasing the utilization of synthetic fibers and have actively explored the adoption of WPC derived from sources like hemp, flax, sisal, jute, or kenaf in various components of their vehicles, encompassing both non-structural and structural

elements to decrease the overall life cycle impacts of an automobile, primarily by decreasing weight and resource usage [4]. The remarkable advantages of WPCs contribute to the development of more efficient, eco-friendly, and visually appealing vehicles. At this point, understanding and identifying the thermal degradation kinetics of such composite panels can be probably critical for optimizing end-product flammability, charring, toxicity, and smoke reduction for the automobile industry [5]. A chief obstacle to understanding thermal degradation mechanism of WPC is that heterogeneous compositions comprise complex lignocellulosic woody biomass, polymer matrix and additives in the structure. To circumvent the complexity of kinetics and thermodynamics of thermochemical conversion, investigating thermal behaviors of materials using thermogravimetry has gained ground in the past decades. Using experimental data from thermogravimetric analysis (TGA) is a common technique for examining the thermally driven processes and it is a widely used approach for studying thermal phenomena and calculating kinetic parameters in thermochemical conversion which relies on observing changes in the weight of materials as they undergo physical and chemical transformations. By this way, valuable insights into the underlying processes of degradation can be provided and key temperatures associated with material degradation, the rate at which degradation occurs, the amount of residual solid left behind (char residue), and the kinetic parameters can be identified. This knowledge is critical in composite materials science where precise control over reaction rates, thermal stability, and product quality is essential. Therefore, the main subject of this paper is to gain a deep knowledge of the thermal degradation of WPCs under air and nitrogen atmosphere from a kinetic point of view. For this purpose, herein degradation mechanism and the kinetics model of wood-plastic composites were analyzed by the thermogravimetric analysis (TGA) and the Coats–Redfern method to provide an essential reference for the degradation mechanisms of such composite structures.

2. An Overview of WPCs

Wood-polymer composites (WPCs) are hybrid materials that combine the benefits of wood fibers or particles with polymer matrices, resulting in a composite material with improved mechanical, thermal, and aesthetic properties [6]. WPCs have gained significant attention in various industries, especially in automotive industry, due to their potential to replace traditional materials such as metals, plastics, or solid wood in specific applications. In the automotive sector, WPCs are utilized for manufacturing automobile parts to enhance performance, reduce weight, and improve sustainability. WPCs find application in various automotive components, including interior trim (such as door panels, dashboard trims and center consoles), exterior components (such as fenders, spoilers, and roof panels) and structural parts (such as seat frames and floor panels) as it can be seen in Figure 1. WPCs are making their mark in the automotive sector, not just as a general trend but through specific, practical applications that improve both vehicle aesthetics and functionality.

For instance, the unique properties of WPCs allow for intricate designs and textures that mimic natural wood while offering the durability and ease of maintenance of plastics when they are used for dashboard panels. It is known that the latest models of certain luxury and eco-friendly vehicles now feature dashboards made from WPCs. Combining the warm, appealing aesthetics of wood with the modern functionality required in automotive interiors. These panels are resistant to scratches and UV radiation, ensuring they maintain their appearance over the vehicle's lifespan. Another specific example use of WPCs is in the construction of seat backs of automobiles. The rigidity and strength of WPCs make them ideal for supporting the backrests of car seats, providing durability and safety. Additionally, the ability to mold WPCs into ergonomic shapes contributes to improved passenger comfort. Some electric vehicle manufacturers have incorporated WPC seat backs to enhance the sustainability of their interiors, reflecting the industry's shift towards environmentally friendly materials.

WPCs for automotive parts typically consist of a combination of wood fibers, such as sawdust or wood flour, and a polymer matrix, commonly a thermoplastic or thermosetting resin. The wood fibers provide reinforcement, while the polymer matrix offers durability and stability [7,8]. The combination of woody biomass and polymers provides WPCs with excellent strength, stiffness, and impact resistance, making them suitable for structural components. Also, utilizing renewable biomass sources and reducing reliance on non-renewable materials makes WPCs a more sustainable choice compared to some traditional materials. Because these composite structures offer several benefits, including reduced reliance on non-renewable energy sources as eco-friendly materials, enhanced energy recovery, decreased emissions of pollutants and greenhouse gases, and the biodegradability of components at the end of their life cycle. However, inherent drawbacks might exist such as susceptibility to moisture absorption leading to strength loss, variations in properties and quality due to cultivation conditions of lignocellulosic woody biomass, limited impact strength, restricted maximum processing temperatures, and inadequate fire resistance [8,9]. The swelling and mildewing of woody biomass caused by water absorption will notably diminish both the mechanical characteristics and lifetime of WPCs [10]. Therefore, balancing the advantages and disadvantages of WPCs in automotive applications requires a comprehensive approach that addresses both material properties and application-specific requirements. Especially, continuously improving the composition of WPCs to enhance their mechanical properties, such as strength, stiffness, and impact resistance, while minimizing their susceptibility to moisture absorption and degradation can involve experimenting with different wood/plastic ratios, additives, and surface treatments. Afterwards, conducting thorough performance testing to validate the suitability of WPCs for automotive applications, including durability, crashworthiness, flammability, and weather resistance can instill confidence in the material's performance and safety standards. It is important to consider that tailoring the design and engineering of automotive components to leverage the strengths of WPCs while mitigating their weaknesses may involve strategic

placement of WPCs in non-critical areas, reinforcement with other materials, or implementing innovative structural designs.

Utilizing advanced manufacturing processes to ensure precise control over material distribution and structural integrity can help mitigate variations in properties and quality often associated with WPCs. Various production techniques, including extrusion, injection molding, compression molding, or a combination of these methods can be used for the industrial scale production of WPCs. The process involves mixing woody biomass with the polymer matrix, followed by shaping the material into the desired form using appropriate molding techniques [11,12].

It should be considered that, a balance between the advantages and disadvantages of wood-plastic composites in automotive applications can be created by adopting a holistic approach that addresses material composition, processing techniques, performance testing, application engineering, lifecycle assessment, and collaboration, by leading to more sustainable and efficient transportation solutions. Conducting a comprehensive lifecycle assessment to evaluate the environmental impact of WPCs throughout their entire lifecycle, from raw material extraction to end-of-life disposal or recycling can identify opportunities for improvement can help minimize environmental drawbacks while maximizing sustainability benefits [13,14]. Overall, wood-polymer composites offer promising opportunities in the automotive industry, providing a balance between performance, sustainability, design flexibility, and cost. Ongoing research and development are expected to further enhance the properties and expand the range of applications for WPCs in automobile parts.



Fig. 1. Automobile components made of WPCs [15]

3. Material and Methods

3.1. Preparation of the Material and Thermoanalytical Measurements

The composite panel obtained from a commercial production plant located in Anatolia region of Turkey were cryogenically grounded to a size below 150 μm and then stored in air-tight containers to use for further analysis. To ensure negligible internal temperature fluctuations within the particles, the selection of this particle size was made based on the assumption of a uniform temperature distribution inside the particles.

Prior to conducting TGA experiments in a thermal analyzer (Hitachi STA 7300), the crucibles and chamber were cleaned using compressed air of exceptional purity. To minimize the influence of

thermal conduction within the sample, approximately 10 mg of WPC sample was placed in an alumina crucible and evenly spread. In addition, blank experiments were conducted to establish reference points and make necessary adjustments to minimize the impact of mass transfer effects. In each experimental trial, sample subjected to heating up to 1000 $^{\circ}\text{C}$ using a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in a non-isothermal mode. Throughout the experiments, measurements were carried out under air and nitrogen atmosphere with a constant flow rate of 100 cm^3/min . The experiments were performed three times to achieve the lowest error and highest accuracy. The data obtained from the TGA measurements were subsequently utilized for subsequent kinetic analyses. To gain more information about the tested material from morphological point of view SEM analysis was performed using Zeiss Supra 40 VP. The mechanical properties were obtained from the company using the average of the three samples.

3.2. Theory and Calculation of the Thermal Degradation

Kinetics

In a typical TGA experiment, the reduction in weight of the sample is monitored over time or temperature, using either constant (isothermal) or changing temperature (non-isothermal) programs [16,17] kinetics refers to the study of chemical reactions or transformations that occur at a constant temperature. By subjecting a material to a controlled temperature environment and monitoring its weight loss or gain over time, TGA allows researchers to determine the reaction rate constants, activation energies, and reaction mechanisms associated with the isothermal process. On the other hand, non-isothermal kinetics involves studying reactions or transformations that occur under changing temperature conditions. In many practical applications, materials are subjected to varying temperature profiles, such as heating, cooling, or thermal cycling. TGA enables the investigation of such dynamic temperature conditions and provides valuable data on the thermal stability, decomposition pathways, and reaction rates of the material over a wide temperature range.

Non-isothermal thermogravimetric kinetic analysis offers several advantages over isothermal kinetics, providing valuable insights into the thermal behavior of materials under dynamic temperature conditions. At first, non-isothermal kinetics closely mimics the actual temperature profiles experienced by materials in various applications, such as heating and hence more accurate understanding of the material's behavior and performance in real-world scenarios can be obtained. Also, non-isothermal analysis enables the identification and analysis of complex reactions occurring during degradation by providing a more detailed understanding of the underlying mechanisms and kinetics. By this non-isothermal way, kinetic parameters, such as activation energy and pre-exponential factor, over a broader temperature range compared to isothermal experiments can be achieved. This comprehensive temperature coverage enhances the accuracy and reliability of the kinetic data, enabling better prediction and control of reaction rates and product formation. Non-isothermal analysis can also provide valuable information about the thermal stability

of materials, including the onset temperature and the decomposition pathways. This knowledge is crucial for assessing the suitability of materials in high-temperature applications and for designing thermal management strategies. Consequently, researchers can optimize the temperature profiles and product quality of the materials by the help of non-isothermal kinetics, since it offers a more realistic representation of practical conditions, a comprehensive understanding of complex reactions, and a wider temperature range for determining kinetic parameters [18–20].

In the context of thermally stimulated processes, the aim of kinetic analysis is to establish mathematical correlations between temperature, degree of conversion, and process rate. An essential practical objective is to estimate material lifetimes and process rates accurately. Reliable predictions hinge upon the application of sound kinetic analysis techniques [21]. There are two primary mathematical methodologies for extracting kinetics data as model-free methods, and model-based methods. Model-based kinetics lies in its ability to provide detailed mechanistic insights, estimate reaction rates, make predictions, compare materials, and optimize experimental design. These benefits contribute to a deeper understanding of the thermal degradation behavior of materials and support informed decision-making in material development and process optimization.

The analysis of thermogravimetry data to determine kinetics involves the application of a mathematical procedure, which begins with the general formula stated below.

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

The conversion can be expressed with the formula given below:

$$\alpha = \frac{(m_o - m_t)}{(m_o - m_f)} \quad (2)$$

At a linear temperature heating rate (β) it can be written as:

$$\beta = \frac{dT}{dt} \quad (3)$$

On the other hand, two different independent functions, namely temperature function ($k(T)$) and fractional conversion function ($f(\alpha)$), defines kinetic expression as provided in Eq. 4:

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

After the rearrangement and integration, the final linearized form of Coats & Redfern model [22] (for $n=1$) is given by:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (5)$$

On the other hand, the model equation has resulted by the following equation for the orders different than unity ($n \neq 1$):

$$\ln \left[\frac{1 - (1-\alpha)^{(1-n)}}{T^2 (1-n)} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (6)$$

For usual reaction at possible temperature, $E/RT \gg 1$. Therefore, the first part of the right hand of Eqs. (5) and (6) is regarded as constant. That's why, a line with slope $-E/R$ and intercept $\ln[AR/\beta E]$ can be obtained by plotting the left hand of Eqs. (5) and (6) with n correctly selected. The more detailed derivation process of the final linearized equations can also be found in the literature. [23–25]. In summary, Eqs. (5) and (6) enable the estimation of kinetic parameters, such as activation energy and pre-exponential factor. Figure 2. summarizes the detailed research procedure and methods of the study.

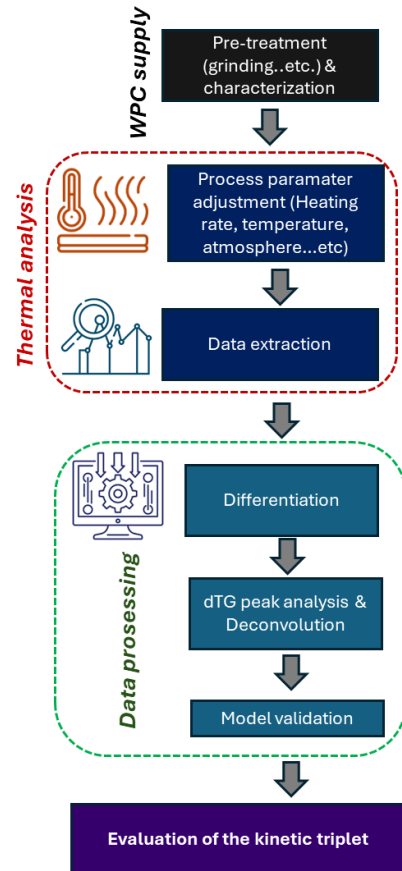


Fig. 2. Flow diagram of the research methodology and experimentation process

4. Results and Discussion

4.1. Characteristics of the Material

Before the thermoanalytical measurements, the mechanical and morphological properties of the composite material were determined to characterize the sample. The as-received sample is shown in Figure 3. The material was fabricated through a batch extrusion process involving wood flour and polypropylene, resulting in laminate sheets produced by a company based in Eskişehir, Turkey. ASTM D792 was performed to measure the density of the WPC material used in the study while ASTM D3039 method was used to determine the mechanical properties, including the determination of tensile strength, tensile modulus, and elastic modulus in the longitudinal and transverse directions.

Moreover, SEM analysis was performed to identify and verify the composite's internal structure, and the resultant micrographs are given in Figure 4. The SEM micrographs of the WPC sample are clear indications of the structural integrity of the composite was observed with an even surface without aggregations of biomass sample inside the polymer matrix. However, it was noticed that some slight cracks were observable in the polypropylene matrix along both the transverse and longitudinal directions of the biomass straw. However, none of the WPC structures showed any clear signs of phase separation, demonstrating the high degree of compatibility between biomass and polypropylene. The effective coverage of woody biomass particles on the smooth surface of polypropylene can be visualized from the SEM micrographs of WPC. Mechanical properties of WPC are seen in the Table 1.

Table 1. Mechanical properties of WPC used in the study

Density (g/m^3)	1.4
Tensile strength- longitudinal (MPa)	41.2
Tensile strength- transverse (MPa)	28.2
Tensile modulus - longitudinal (MPa)	>3200
Tensile modulus- transverse (MPa)	>2250
Elasticity modulus-longitudinal (N/mm^2)	>3100
Elasticity modulus- transverse (N/mm^2)	>2100

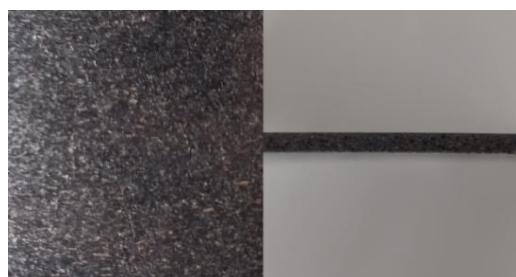


Fig. 3. Upper surface (left) and cross-section (right) of WPC sheet

4.2 Thermogravimetric Analysis

According to Figure 5, the first derivative TG curve (dTG) of WPC under air atmosphere exhibited two thermal decomposition peaks. The initial peak occurred at 359 °C, followed by a secondary and tertiary peak that appeared at 401 and 510 °C, respectively. The rate of decomposition was less than 0.1%/°C when the temperature was above 555 °C. As a result, the temperature range of 223–555 °C was identified as the decomposition phase of WPC. Within this range, approximately 86.5 wt.% of the mass was lost. After heating the sample up to 1000 °C, a solid residue around 13 wt. % remained. On the other hand, pyrolytic decomposition of WPC under inert atmosphere is shown in Figure 6. and showed narrower temperature range (between 197–483 °C) with the maximum weight loss rate being observed at 456 °C. After heating the sample up to 1000 °C, a solid residue around 16 wt. % remained while approximately 78.2 wt.% of the mass was lost at the end of the main degradation zone. It can be concluded from the comparison of the results obtained in different atmospheres tendencies of mass loss and the rate of the

mass loss changed considerably. The thermal degradation profiles reflected the degradation of PP matrix and lignocellulosic matrix. But it is also worth to mention that the fillers and the minor additives that are added during the production, to enhance interaction between polymer and lignocellulosic biomass, can be effective on the thermal stability of the resultant composite material by changing the chain mobility of the polymer matrix.

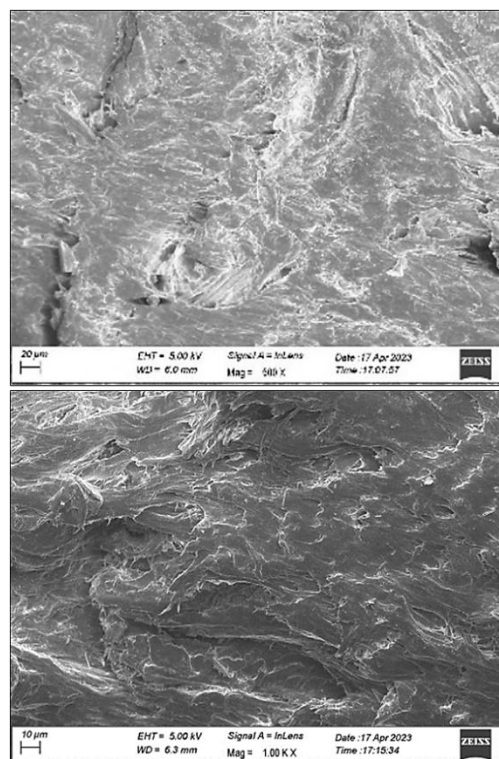


Fig. 4. SEM micrographs using magnifications of 500 and 1000x

Gaussian multi-peak fitting function has been used to extract the reaction zones associated to obtain accurate values of the kinetic triplet using dTG profiles as Given in Figure 7. By this way, mass loss contributions of each kinetic sub-zone were isolated. Each distinctive WPC sample's dTG thermogram underwent deconvolution to evaluate the procedure's reliability. After averaging the generated peaks, the standard deviations of each peak were determined to evaluate the reliability of the outcomes. According to the obtained results and peak fitting quality, Gaussian function has been successfully employed in dealing with multistep kinetics of WPC both in oxidative and pyrolytic decomposition. The function was used to match the dTG peaks of the active thermal degradation phase based on the aforementioned three distinctive peaks. To put it other words, the complex devolatilization of WPC was deconvoluted into three peaks for both oxidative and pyrolytic degradation using the Gaussian function. Table 2 provides a summary of the peak information, including the initial, maximum and final points together with full width at half maximum (FWHM) Thermal degradation processes under air and nitrogen atmosphere showed high coefficient of determination (R^2) values of 0.9902 and 0.9815, respectively.

According to the first curves which are given in Figure 7, polypropylene degradation in air showed an earlier and more pronounced weight loss compared to nitrogen. The weight loss at the first and second peak exhibited a steeper slope due to the oxidative decomposition when it was compared with the pyrolytic degradation under nitrogen atmosphere. Peaks were further correlated with the reaction zones and given as the equivalent reaction 1, 2, 3 in the following zones for both in air and nitrogen atmospheres.

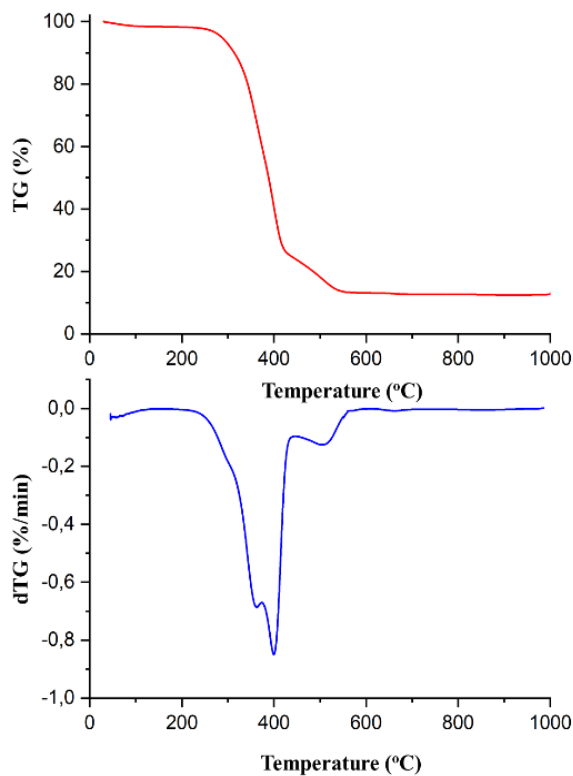


Fig. 5. TG and dTG thermograms of WPC under oxidative atmosphere

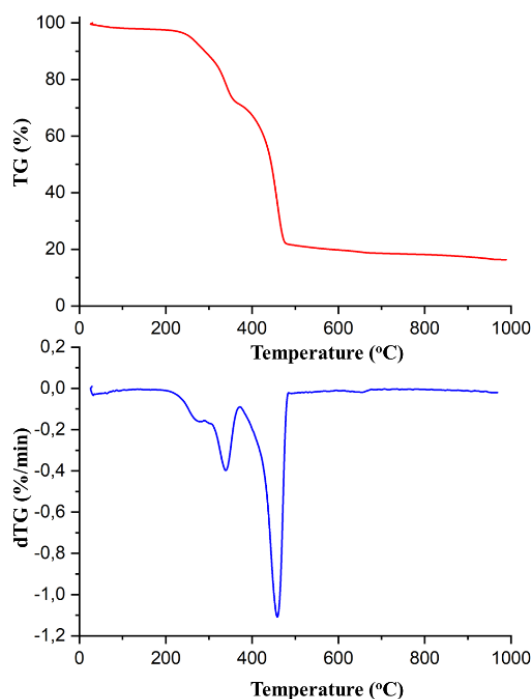


Fig. 6. TG and dTG thermograms of WPC under air atmosphere

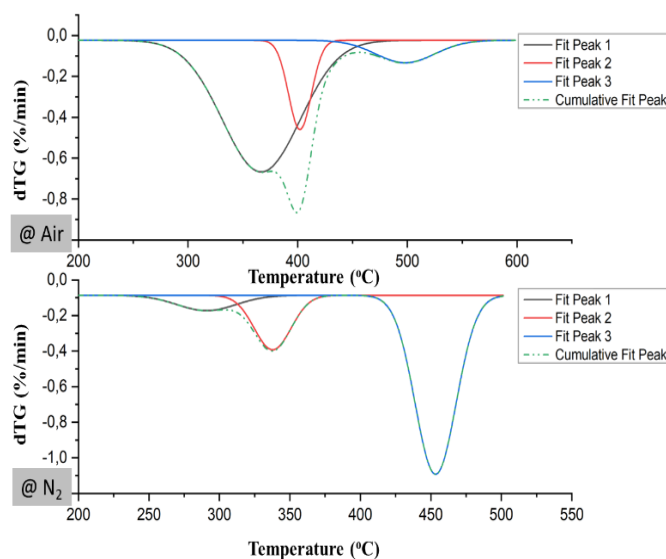


Fig. 7. Peak deconvolution for the dTG thermograms air and inert atmosphere

4.3. Kinetic Analysis

According to different reaction orders as it was shown in Figure 8. According to the Figure 8, each sub-temperature range had a different reaction order. Keeping in mind that the order of reaction refers to the mathematical relationship between the concentrations of reactants and the rate of reaction, as the temperature changes the dependency of the concentration and the radical formation tendency changed. Table 3 shows the activation energy, frequency factor, and regression coefficient values together with the reaction order for the each devolatilization zone during pyrolysis and

combustion. Each reaction orders performance was evaluated by assessing the correlation coefficient as it may be seen in the Table 3. The activation energy value signifies the minimum energy required to initiate the reaction; a lower activation energy value suggests a higher likelihood of the sample reacting more promptly. Conversely, higher activation energy values indicate greater stability of the sample [26]. According to the results initial temperatures of thermal decomposition exhibited higher activation energy values for both atmospheres compared to the second reaction stages. According to calculated activation energies, it was

determined that the energy barrier to start the thermal degradation under nitrogen is slightly than that of oxidative degradation. Oxidative thermal decomposition had an activation energy value of 227 kJ/mol while pyrolytic degradation had 229 kJ/mol. This may indicate that the presence of an oxidizing agent provides additional reaction pathways by which WPC can decompose. These pathways may involve intermediate species formed through oxidation reactions, which can lead to lower activation energies compared to pathways in pyrolytic decomposition. Moreover, oxidative thermal decomposition can increase the reactivity of the material compared to pyrolytic decomposition by the help of oxygen-induced reactions. This increased reactivity can facilitate the breaking of chemical bonds and slightly decrease the activation energy required for decomposition. When it comes to second temperature zone, activation energy values decreased to 120 kJ/mol and 92 kJ/mol for oxidative and pyrolytic thermal decomposition, respectively. A decrease in activation energy during the second temperature zone of thermal decomposition indicates changes in reaction pathways, increased reactivity, radical interactions, or phase transitions. This lower activation energy values implied that the molecules of the WPC material are more easily activated at intermediate temperatures, indicating increased reactivity. This could be due to the breaking of stronger bonds or the rearrangement of molecular structures, making them more susceptible to decomposition. However, the last sub-temperature zones that were characterized by higher degree of conversion at higher temperatures showed an unsimilar behavior which led to increase in activation energy values up to 242 kJ/mol and 191 kJ/mol. This implied that the decomposition process may lead to the formation of stable species that require more energy to further react at higher temperatures. These stable intermediates may hinder the thermal decomposition process, leading to an increase in activation energy. To put it another words, thermal decomposition products of WPC may become thermally stabilized at higher temperatures, requiring more energy to overcome the energy barriers for further decomposition. This can lead to an increase in activation energy as the temperature rises at the last temperature zone. Moreover, changes in the physical properties of the material, such as charring or the formation of barriers to diffusion, can impede the decomposition process at higher temperatures. Considering all the numerical values related with the kinetics, the regression coefficients of the Coats and Redfern model (R^2 value) were obtained between 0.9809 and 0.9997. These regression coefficients were sufficiently high enough indicating that the Coats and Redfern model was compatible with the experimental TGA data for obtaining the activation energies of the samples under inert and oxidative conditions. Upon analyzing the activation energies across the entire range of conversion, to comprehend the mechanism underlying the thermal degradation, it was deduced that the values exhibited a tendency to fluctuate relative to the sub-temperature zones [27].

Table 2. Results of the non-linear curve fitting at different atmospheric conditions

Atmosphere	Curve fitting parameters		
@ Air	Peak 1	T_i	221.9
		T_{max}	366.7
		T_f	469.5
		FWHM	83.2
	Peak 2	T_i	362.9
		T_{max}	402.0
		T_f	432.1
		FWHM	24.4
	Peak 3	T_i	434.3
		T_{max}	498.1
		T_f	554.6
		FWHM	63.5
	Adj. R^2		0.9902
@ N ₂	Peak 1	T_i	197.1
		T_{max}	290.8
		T_f	332.6
		FWHM	49.1
	Peak 2	T_i	295.1
		T_{max}	337.8
		T_f	371.8
		FWHM	30.6
	Peak 3	T_i	404.2
		T_{max}	453.3
		T_f	484.2
		FWHM	34.1
	Adj. R^2		0.9815

Table 3 also shows the pre-exponential values of each sub-temperature zone related with the thermal degradation under air and nitrogen atmosphere. The fluctuations observed in the pre-exponential factors as a function of conversion degree can be ascribed to alterations in reaction chemistry and the formation of complex species. Typically, pre-exponential factors with values below 10^9 s⁻¹ are associated with surface reactions in reaction kinetics. When reactions are independent of surface area, a low pre-exponential factor signifies the presence of a tightly bound junctional complex, often referred to as a closed complex. Conversely, pre-exponential factors with values equal to or greater than 10^9 s⁻¹ suggest the presence of a loosely bound simple complex, also known as a junctional complex. Additionally, higher pre-exponential factor values indicate greater sensitivity within a reaction temperature range [28–30].

According to the results all the values of pre-exponential factor were found higher than 10^9 s⁻¹. The values indicated high index for intermolecular collisions and simple complex reaction mechanism [31]. Particularly, the activated complex may be limited in rotation compared to the initial reagent when the value of the values was between 10^{10} and 10^{12} s⁻¹ [32]. This was the condition of the initial sub reaction zones of oxidative and pyrolytic thermal decomposition together with the second sub-zone of oxidative decomposition.

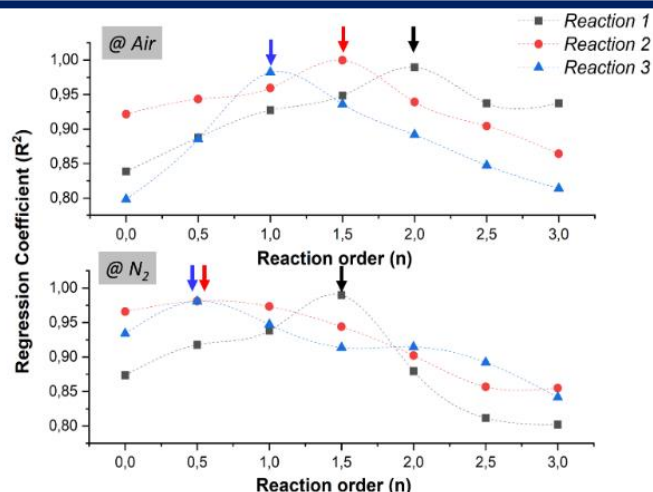


Fig.8. Estimation of the reaction order for the oxidative and pyrolytic degradation of WPC

Table 3. Kinetic parameters for the thermal degradation

@ Air	Reaction	n	R ²	E (kJ/mol)	A (1/s)
	Peak 1	2.0	0.9896	227.47	3.62x10 ¹²
	Peak 2	1.5	0.9997	119.90	4.60x10 ¹⁰
	Peak 3	1.0	0.9890	241.77	4.60x10 ⁹
@ N ₂	Reaction	n	R ²	E (kJ/mol)	A (1/s)
	Peak 1	1.5	0.9896	229.51	1.05x10 ¹³
	Peak 2	0.5	0.9809	92.37	2.98x10 ⁹
	Peak 3	0.5	0.9810	191.30	3.80x10 ⁹

5. Conclusions

The Coats–Redfern method was used to perform kinetic analyses at various heating atmospheres for the prediction and understanding of the reaction mechanism of WPC degradation. The weight loss patterns observed in WPC sample during thermal decomposition under air and nitrogen atmosphere indicated that WPC structure is highly susceptible to thermal degradation and the atmosphere. Empirical findings revealed notable distinctions in the thermal characteristics of WPC under oxidative and inert atmosphere despite having the same number of thermal degradation zones. The thermal degradation process of WPC under air atmosphere exhibited prolonged temperature range compared to that of pyrolytic degradation under nitrogen atmosphere. Results indicated that thermal degradation of the structure is involved in multi-step degradation reactions and such complex process is then separated into three temperature zones. Utilizing thermal analysis assisted in the prediction of forthcoming experiments by proposing ideal experimental parameters, including heating rates, sample dimensions, and intervals for data acquisition. All these findings can offer foundational and theoretical backing for implementing precautionary measures against the occurrence of thermal degradation and fire prevention studies for WPCs.

Nomenclature

α	: degree of conversion
β	: thermal ramp rate (°C/min or K/min)
A	: pre-exponential factor (1/s)
E	: activation energy (kJ/mol)
FWHM	: full width at half maximum.
R	: universal gas constant
R ²	: coefficient of determination/ regression coefficient
t	: time (sn)
T	: temperature (K or °C)
T _i	: initial temperature (K or °C)
T _{max}	: maximum peak temperature (K or °C)
T _f	: final temperature (K or °C)
n	: order of reaction
m _o	: initial weight (mg)
m _t	: instantaneous weight (mg)
m _f	: final weight (mg)

Conflict of Interest Statement

There is no conflict of interest in the study.

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