

Kinetic Analysis of Thermal Degradation of Acrylonitrile Butadiene Styrene (ABS) for its Use in Electrical Appliances

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ABSTRACT: This work investigates the kinetic studies of thermal degradation of Acrylonitrile Butadiene Styrene (ABS) terpolymer. A complete thermal degradation profile of commercially available ABS plastic was recorded at multiple heating rates (5, 10, 15, and 20°C min⁻¹) from ambient temperature to 1000°C under N₂ (100 mL min⁻¹) atmosphere. The maximum degradation (> 90%) of ABS polymer was observed from 360 – 524°C. The effect of heating rates on the thermal stability of ABS polymer and derivative thermogravimetric (DTG) curves was also examined. Different isoconversional approaches such as Flynn-Wall-Ozawa (FWO) and Kissinger were used for the kinetic considerations of thermal data to calculate frequency factor (*A*), activation energy (*E_a*), and order of degradation reactions (*n*). The activation energy values evaluated by FWO and Kissinger methods were observed to be 107.36 kJ mol⁻¹ and 111.28 kJ mol⁻¹, respectively attributed to the preferred use of ABS polymer in electrical appliances.

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I. INTRODUCTION

Acrylonitrile butadiene styrene, commonly known as ABS, is a widely used thermoplastic and engineering polymer composed of three monomers: butadiene, styrene, and acrylonitrile, as indicated by its name (Fig. 1). ABS is one of the most important polymers in the field of chemistry due to its numerous structural applications and remarkable physical properties, which include high rigidity, high tensile strength, and resistance to chemical abrasion and staining. These characteristics make it extremely useful for various industrial applications¹. The chemical formula for ABS is $(C_8H_8 \cdot C_6H_6 \cdot C_3H_3N)_n$, indicating that it consists of three primary elements: carbon, hydrogen, and nitrogen, which are present in different combinations and quantities to form ABS.

Acrylonitrile butadiene styrene (ABS) is a widely used thermoplastic polymer^{2,3}, but it has several limitations that restrict its industrial applications. Its low melting point makes it unsuitable for high temperatures and certain medical uses, like implants. ABS also has poor solvent properties and is not resistant to UV radiation, which can lead to degradation upon exposure. Moreover, it is a poor electrical conductor, limiting its use in devices requiring good conductivity. ABS can combust and release toxic substances at higher temperatures, contributing to air pollution. It is also prone to stress cracking and scratching. Despite these drawbacks, ABS is popular due to its favorable mechanical and electrical properties. With over 6,000 grades available, it is versatile and cost-effective for various applications, especially in the automotive industry, where it is used for components like dashboards and door handles⁴. In the electrical and electronic sectors, ABS is found in household appliances, computers, and mobile devices⁵. When examining the properties of polymers, thermal stability is crucial as it reflects how a material maintains its structure and function under heat stress. Thermal stability defined as the temperature range within which a material can withstand degradation. It is influenced by the size of the atoms, the strength of intermolecular forces, and the atoms' electronic configuration. Typically, larger atoms lead to decreased bond dissociation energy, lowering thermal stability. Thus, thermal sta-

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bility is directly proportional to bond strength and inversely proportional to atom size. This property is vital in engineering and the electrical industry, particularly for high-density energy storage, as it helps determine suitable materials for specific applications. For instance, materials with low thermal stability cannot be used in electrical appliances that operate at high temperatures^{6,7}.

Thermal analysis of polymers is a traditional chemical technique used to evaluate their physical and chemical properties, determining their suitability for electrical and engineering applications. This analysis also investigates aging, phase transitions, environmental effects, additive impacts, and overall durability. Key techniques in thermal analysis include Differential Scanning Calorimetry (DSC), Thermomechanical Analysis (TMA), Dynamic Mechanical Analysis (DMA), and Thermogravimetric Analysis (TGA). These methods collectively provide essential insights into the physical properties of polymers⁸.

The thermal degradation of ABS polymer has been studied both individually and in blends with other materials^{9,10}. Almeida Neto et al.¹¹ examined the thermal breakdown of the acrylonitrile butadiene styrene (ABS) terpolymer in a variety of gas environments as determined by thermogravimetric analysis. Significant products resulting from the pyrolysis of ABS have been identified. Yang¹² assessed the activation energies (E_a) for isothermal heating of ABS resin under different gas conditions using Flynn and Freeman's models. The ABS resin experienced dynamic heating with an activation energy of $42.0 \text{ kcal mol}^{-1}$. Fonseca et al.¹³ utilized isothermal and dynamic thermogravimetric techniques to calculate the apparent activation energy and assess the thermal degradation of acrylonitrile-butadiene-styrene (ABS) and copolymers made of polystyrene (PS), polybutadiene, polyacrylonitrile (PAN), and styrene-acrylonitrile (SAN). They found that all three polymers—PAN, SAN, and ABS—lose some acrylonitrile monomers during degradation. Grafting butadiene onto SAN stabilizes its structure, while the initiation of aromatic synthesis in ABS occurs at a lower temperature than in SAN, which destabilizes SAN. Munir et al.¹⁴ reported that their experimental strategy identified numerous volatile chemicals produced during thermal degradation, which were removed by nitrogen gas flow ($20 - 30 \text{ mL min}^{-1}$), potentially slowing further breakdown. The temperatures used mimic typical industrial processes and may reflect conditions found early in a fire. They also observed that higher acrylonitrile content in styrene-acrylonitrile polymers enhances styrene production during degradation,

explaining the differing styrene emissions from two ABS plastics. Recent proposals have also outlined the main degradation pathways for ABS¹⁵. Additionally, there is new research on the thermal characterization of neat ABS terpolymer from various manufacturers¹⁶.

This study aims to investigate the thermal degradation kinetics of Acrylonitrile Butadiene Styrene (ABS) plastic terpolymer. Specifically, it focuses on determining the rate at which ABS degrades under various temperatures. This information is essential for understanding the long-term performance and lifespan of ABS in electrical appliances where heat is generated. To achieve this, a detailed thermal degradation profile of commercially available ABS polymer is recorded at various heating rates (5, 10, 15, and 20°C per minute) and examined up to 1000°C in a nitrogen atmosphere. The effects of heating rates on the thermal stability of the ABS polymer, as well as the derivative thermogravimetric (DTG) curves are also investigated. Various isoconversional methods, including Flynn-Wall-Ozawa (FWO) and Kissinger, were employed for the kinetic analysis of the thermal data, allowing for the calculation of the frequency factor (A), activation energy (E_2), and the order of the degradation reactions (n). By examining the degradation kinetics, we can predict how ABS components will behave over time and under different operating conditions. This knowledge can assist manufacturers in designing more durable and reliable appliances, as well as inform decisions about material selection and end-of-life management.

II. MATERIALS AND METHODS

A. Material and Measurements

Synthetic polymer Acrylonitrile Butadiene Styrene (ABS) provided by Shin-Etsu Chemical Co. Ltd. Thermogravimetric data of ABS was recorded under N_2 (100 mL min^{-1}) in ramp mode on a Q-500 thermal analyzer (TA Instruments, USA). TG Data was recorded on five different heating rates; 5, 10, 15, 20, and $30^\circ\text{C min}^{-1}$. The acquired data processed using Universal Analysis 2000 (TA Instruments, USA).

B. Kinetic Studies

Several kinetic models are available for analyzing thermal degradation data, including ASTM standard, Coats-Redfern, and isoconversional methods, each with distinct features, suitability, advantages, and limitations. A comparison of these methods is provided in Table I. There are various approaches for analyzing isoconversional solid-state motor data derived from thermo-

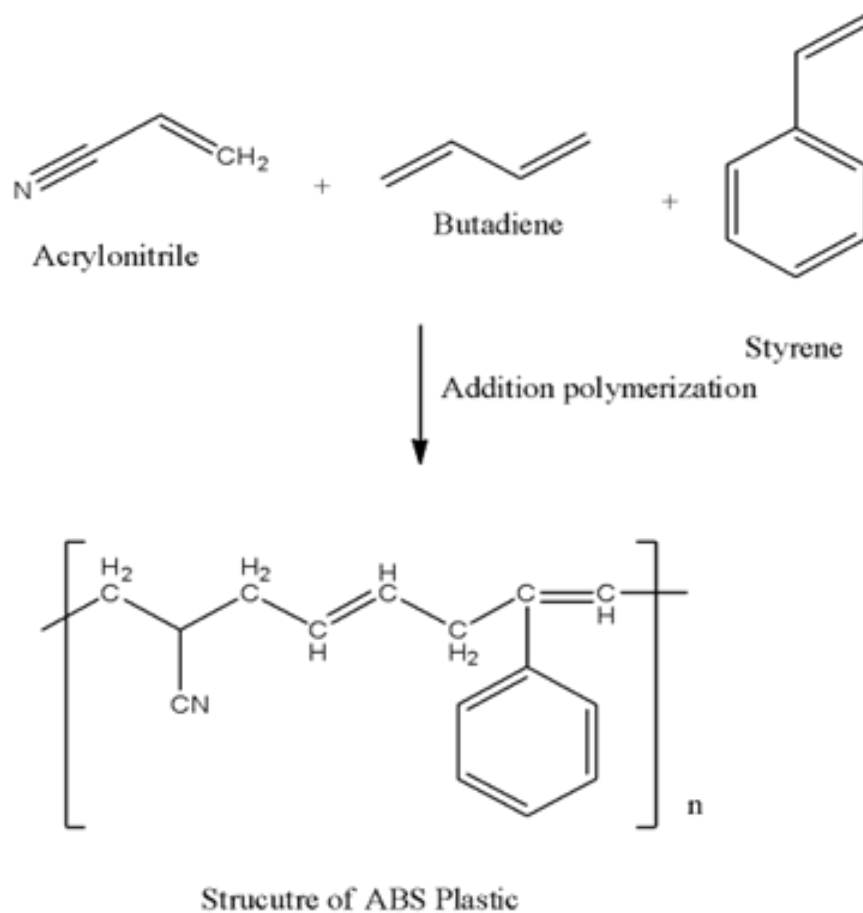


FIG. 1: Polymerization of Acrylonitrile and Styrene in the presence of Butadiene to form ABS.

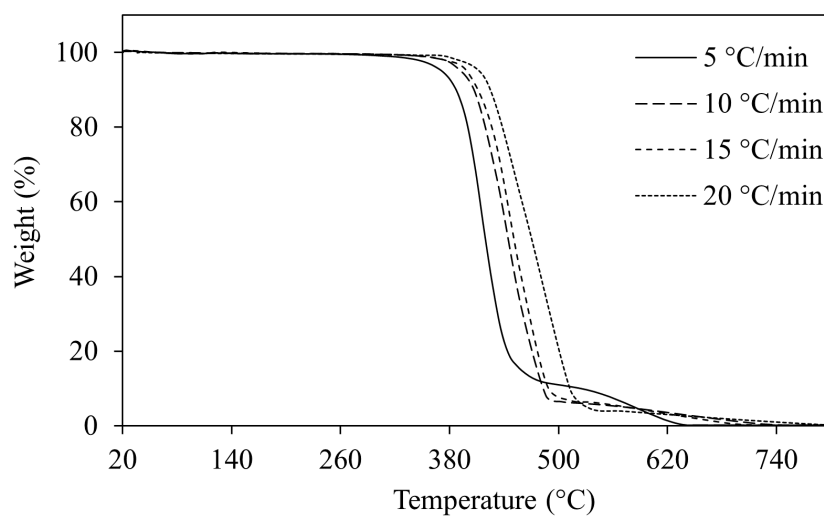


FIG. 2: Overlay of TG curves of ABS at multiple heating rates.

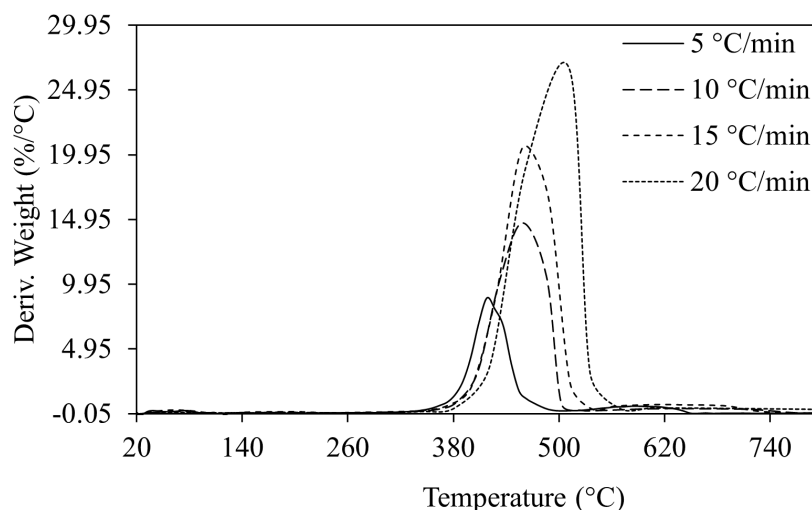


FIG. 3: Overlay of DTG curves of ABS at multiple heating rates.

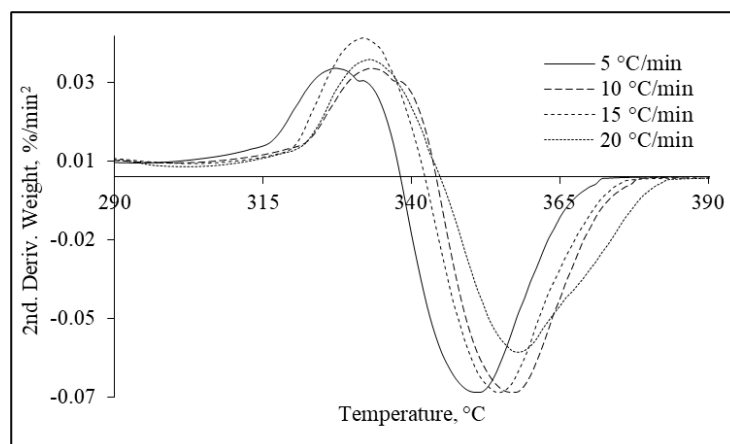


FIG. 4: Overlay of 2DTG curves of ABS at multiple heating rates.

gravimetric analysis (TGA). However, the Flynn-Wall-Ozawa (FWO) method and Kissinger's approach were used in this work to study the kinetics of thermal degradation of ABS (Acrylonitrile Butadiene Styrene). These methods enable the determination of activation energy (E_2) without requiring the assumption of a specific reaction model. Known for the complex degradation mechanism of acrylonitrile butadiene styrene (ABS), which may involve multiple competing reactions, this model-free approach is advantageous as it minimizes potential errors associated with predefined reaction orders. On the other hand, alternative approaches such as the Coats-Redfern method and ASTM standard kinetic models are discussed in the literature but are not

employed in this study. The Coats-Redfern method assumes a single reaction model, which may not accurately capture the complexity of ABS decomposition. Similarly, while ASTM methods are widely accepted, they are typically limited to a single heating rate, which restricts their applicability for thorough kinetic analysis.

Moreover, the FWO and Kissinger methods are widely used in the literature for analyzing the thermal degradation of polymers, making it easier to compare our findings with existing data^{17,18}. Although these methods do not provide detailed insights into the reaction mechanism, the primary focus of this study is to determine the overall kinetics of ABS degradation. The FWO technique assumes that $\ln \beta$ and $1/T$ are lin-

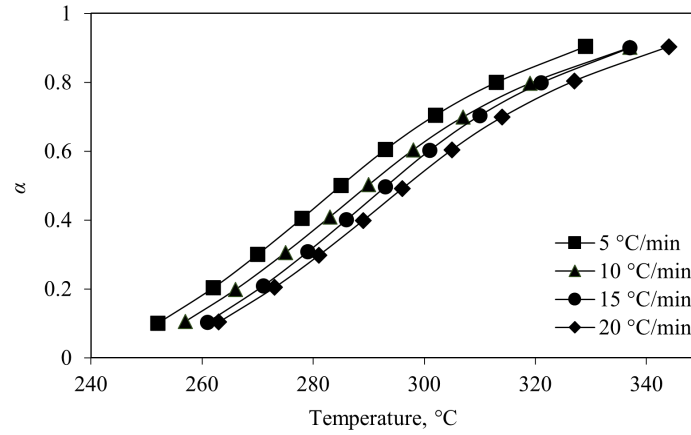


FIG. 5: α vs. T graph for the thermal degradation of ABS at multiple heating rates.

ear in the DTG curve at various heating rates and is based on the premise that the rate of thermal degradation response changes purely on temperature for a given quantity of conversion (α). A straight-line graph and the value of E_α are between $\ln\beta$ and $1/T$ for a given value of α and at various heating rates. To calculate the slope of this graph, Eq. 1 is used.

$$\ln\beta = \frac{AE_a}{Rg(\alpha)} - 5.331 - 1.052 \frac{E_a}{RT} \quad (1)$$

where β referred to as the heating rate; A is the pre-exponential factor; R in the equation represents the general gas constant and T represents the temperature at α . In the above equation, α is calculated by the given relation in Eq. 2;

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

In Kissinger's approach, the temperature of maximum deflection in the DTG thermogram was believed to be the same temperature as the reaction rate. Kissinger's method uses the following equation (Eq. 3).

$$\ln \frac{\beta}{T_m^2} = -\frac{E_a}{RT_m} + C \quad (3)$$

For constant conversions, a plot of $\ln(\beta/T_m^2)$ versus $1000/T_m$ gives the E_a at that conversion. The following equation is used to determine the order of reaction n using the Kissinger method for determining the shape

index.

$$S = \frac{\left[\left(\frac{d^2\alpha}{dt^2} \right) \right]_L}{\left[\left(\frac{d^2\alpha}{dt^2} \right) \right]_R} \quad (4)$$

The values of $(d^2\alpha/dt^2)_L$ and $(d^2\alpha/dt^2)_R$ are obtained from the 2DTG curve, where the subscripts "L" and "R" denote data on the left and right sides of the 2DTG peak, respectively. The value of "S" aids in the calculation of n using the Equations 5 and 6.

$$n = 1.88 S \quad (S \geq 0.45) \quad (5)$$

$$n = 1.26 S^{0.5} \quad (S \leq 0.45) \quad (6)$$

The Eyring-Polanyi equation (7) is used to investigate the thermodynamic parameters such as Gibbs free energy (G), enthalpy (H), and entropy (S) for thermal degradation.

$$k = \frac{k_a T}{h} e^{\frac{\Delta G}{RT}} \quad (7)$$

By incorporating the value of ΔG in the above equation, the following Eq. 8 can be obtained to calculate the enthalpy and entropy values.

$$\ln \frac{K}{T} = -\frac{\Delta H}{R} \times \frac{1}{T} + \ln \frac{K_a}{h} + \frac{\Delta S}{R} \quad (8)$$

TABLE I: A comparison of kinetic models for analyzing thermal degradation of ABS.

Method	Type	Suitability for ABS Degradation	Advantages	Disadvantages
ASTM Standard	It assumes specific reaction models, often based on order of the reaction.	Limited suitability due to its complex, multi-step degradation.	Widely accepted, industry-standard	Limited to single heating rates
	Integral method	Limited suitability due to its complex, multi-step degradation.	Relatively simple to apply	May not accurately represent complex degradation
Coats-Redfern	assumes specific reaction mechanism	Highly suitable due to its complex degradation.	Activation energy at multiple conversion points	Requires multiple heating rates
FWO	Isoconversional Model-free	Highly suitable due to its complex degradation.	Simple and widely used for peak analysis	Does not provide detailed mechanistic information.
Kissinger	Isoconversional Model-free			

Here K is the rate constant, K_B is the Boltzmann constant, ΔH is the activation enthalpy, R is the gas constant, T is the absolute temperature, h is the plank constant, and ΔS is the entropy of activation. Plotting $\ln \frac{K}{T}$ vs. $\frac{1}{T}$ yields a straight line. For a given thermal degradation reaction, the slope of the straight line gives the H value, while the intercept provides the S value.

III. RESULT AND DISCUSSION

A. THERMAL DEGRADATION STUDIES

Multiple heating rates were applied to investigate the thermal degradation behavior of ABS over the temperature range of 20 – 1000°C. TGA data of ABS revealed a single stage of degradation. Almost 92% of the total mass of ABS is degraded in this single step. The overlay TG curve for ABS is shown in Fig. 2 and shows that degradation temperature values increase by increasing the heating rate (β). Similarly, overlaid DTG curves are given in Fig. 3, and these curves also show that the degradation rate increases with the higher heating rate values. This increase in thermal stability may be due to the unequal distribution of heat to the sample at higher heating rates. 2DTG curve that is used to calculate the order of reaction (n) is depicted in Fig. 4. The values of initial, maximum, and final degradation temperatures (T_{d_i} , T_{d_m} , and T_{d_f} , respectively) are given in Table I. For ease of understanding, the data recorded at 10°C min⁻¹ is presented in Table I, along with the mass loss values for the single degradation step.

The initial temperature for the major thermal degradation (T_{d_j}) of ABS was 360°C, while the final degradation temperature reached 524°C when subjected to a heating rate of 10°C per minute. The first step of degradation showed a significant mass decrease of ap-

proximately 92 percent. The temperature of maximum degradation (T_{d_m}) for this initial significant degradation phase of ABS was found to be 458°C. This indicates that ABS has considerable thermal stability, as demonstrated by the peak breakdown temperature (T_{d_m}) during its major degradation phase (refer to Table II). Furthermore, the plots of α against temperature (T) for the first and second steps of thermal degradation of ABS, illustrated in Fig. 5, reveal similar degradation patterns across all heating rates.

B. KINETICS AND THERMODYNAMICS ANALYSIS

To analyze the various kinetic parameters, the FWO and Kissinger isoconversional methods were utilized. The frequency factor (A) and activation energy (E_a) are two important parameters for these kinetic studies. Kissinger's method was employed to determine the order of degradation reactions (n). The FWO approach was used to assess the breakdown of both phases at various transformation levels (ranging from 0.1 to 0.90 in increments of 0.1). In this context, the FWO method is considered the most reliable approach. For the initial stage of thermal degradation of ABS, the activation energy value was found to be 107.36 kJ mol⁻¹ (as shown in Table 2). The activation energy obtained in this study aligns with the values of 11.43 kJ/mol and 105 kJ/mol reported by Bano et al.¹⁷ and Poli et al.¹⁹, respectively, using the isoconversional (FWO) method. The FWO plots of $\ln(\beta)$ against $1000/T$ at various α degrees (0.1-0.9) for each thermal degradation step of ABS are presented in Fig. 6.

The Kissinger technique is used to evaluate the T_{d_m} at each heating rate, and the values of E_a are calculated by the slope of the straight-line graph between $\ln(\beta/T_m^2)$ and $1000/T_m$ as shown in Fig. 7. The E_a

TABLE II: Average thermal decomposition temperatures, mass loss (%), and char yield (%) of ABS recorded at multiple heating rates.

Sample	Step	T _{did} (⁰ C)	T _{d m} (⁰ C)	T _{d f} (⁰ C)	Weight loss % at T _{d f}	Char yield Wt. (%)
ABS	I	360	458	524	92.18	0.13 at 800°C

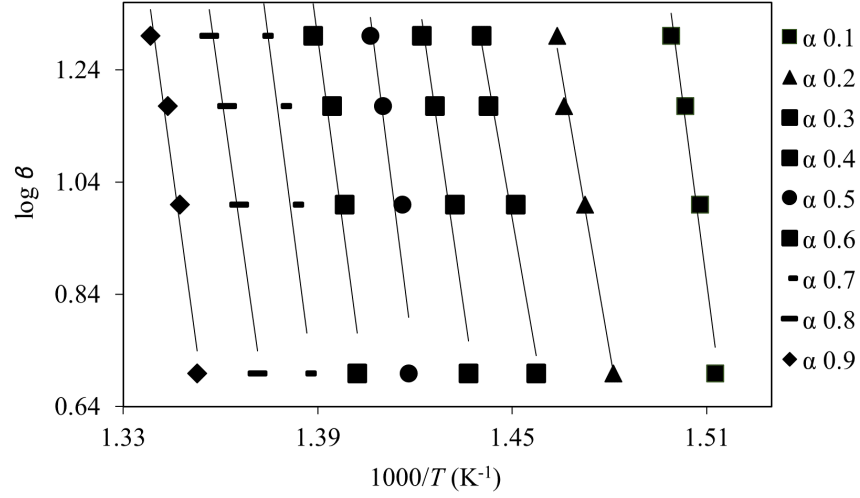
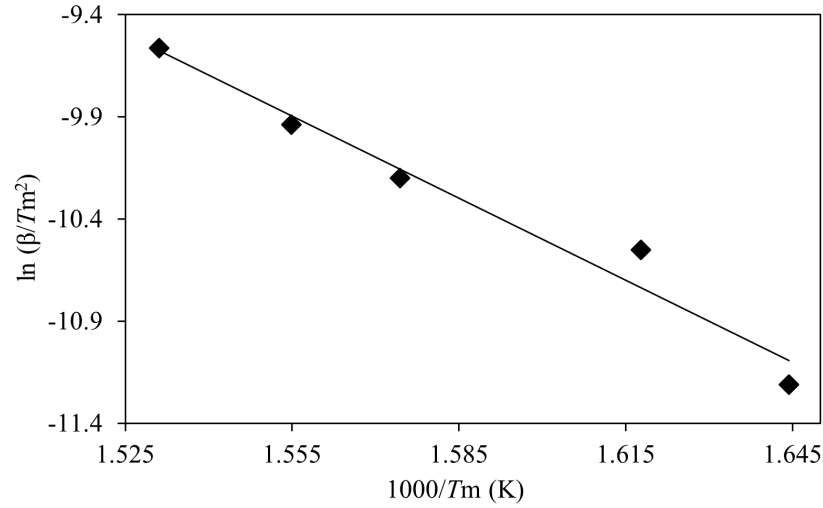
FIG. 6: FWO plot between $\log \beta$ and $1000/T$ (K^{-1}) at several degrees of conversion for ABS.FIG. 7: Kissinger plot for the calculation of E_α of ABS at several β values.

TABLE III: Thermal kinetics and thermodynamic parameters of ABS.

Sample	Method	Step	n	E_a (kJ mol^{-1})	$\ln A$	ΔH	ΔS	ΔG	IPDT	ITS
ABS	FWO	I	-	107.36	17.84	101	-122	190.42		
	Kissinger	I	1.02	111.28	17.63	105	-123	195.41	396	0.53

value determined for the first important step degradation of ABS determined was $111.28 \text{ kJ mol}^{-1}$. The E_2 value resulting from the Kissinger method is very similar to those obtained from the FWO method. In each heating phase, ABS exhibited first-order kinetics, consistent with the predictions of Kissinger's decomposition method. A similar, E_2 value (134 kJ mol^{-1}) has been determined for ABS's degradation by Yang et al.¹², using Freeman and Carroll's isothermal approaches. The study's findings further confirm that ABS demonstrates multi-step degradation kinetics, highlighting the necessity for model-free methods such as FWO and Kissinger for thorough analysis. The kinetic results obtained from the Kissinger method are provided in Table II.

The thermodynamic parameters, including the change in Gibbs free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS), were calculated using thermogravimetric (TG) data for acrylonitrile-butadiene-styrene (ABS) as shown in Figure 1. These parameters are summarized in Table 3. Thermal stability is assessed by examining the area under the TG curves rather than solely relying on degradation temperatures. In this context, two important thermal characteristics are the intrinsic thermal stability (ITS) and the integral procedural decomposition temperature (IPDT). For ABS, the mean ITS value was found to be 0.53 , while the mean IPDT value reached 396°C . These substantially high IPDT readings indicate that ABS possesses good thermal stability.

IV. CONCLUSION

In conclusion, this study provides a comprehensive analysis of the thermal degradation kinetics of Acrylonitrile Butadiene Styrene (ABS) polymer under a nitrogen atmosphere. TGA indicated a single-step degradation process ($360^\circ\text{C} - 524^\circ\text{C}$) characterized by a significant mass loss of 92%. The influence of heating rates on the thermal stability and derivative thermogravimetric (DTG) curves was systematically explored, highlighting the thermal behavior of ABS. The activation energy values for thermal breakdown assessed using the Flynn-Wall-Ozawa and Kissinger isoconversional models demonstrated that ABS resin underwent complete degradation when heated to high temperatures. Other thermal stability parameters also confirmed that ABS is a thermally stable material suitable for use at elevated temperatures. Its higher stability makes ABS an ideal choice for applications in electrical appliances. Additionally, an understanding of degradation behavior could enhance predictive maintenance strategies, ensure regulatory compliance, and optimize recycling methods for ABS-based components.

DECLARATION OF COMPETING INTEREST

The authors have no conflicts to disclose.

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