

## INFLUENCE OF EGGSHELL-DERIVED $\text{CaCO}_3$ ON THE THERMAL DEGRADATION AND KINETICS OF PVC

Nur Aisya Affrina Mohamed Ariffin<sup>1</sup>, Jiahe Poy<sup>1</sup>, Guo Ren Mong<sup>2</sup>, Keng Yinn Wong<sup>1,3</sup>, William Woei Fong Chong<sup>1,3,\*</sup>

<sup>1</sup> Faculty of Mechanical Engineering, Universiti Teknologi Malaysia (UTM), 81310 Johor Bahru, Johor, Malaysia;

<sup>2</sup> School of Energy and Chemical Engineering, Xiamen University Malaysia, 43900 Sepang, Selangor Darul Ehsan, Malaysia

<sup>3</sup> Institute for Sustainable Transport (IST), Universiti Teknologi Malaysia (UTM), 81310 Johor Bahru, Malaysia

\* Corresponding author: william@utm.my

### ABSTRACT

The increasing demand for sustainable polymer additives has heightened interest in waste, like eggshell, which is rich in calcium carbonate ( $\text{CaCO}_3$ ). However, its impact on the thermal decomposition behaviour of polyvinyl chloride (PVC) remains not fully understood. This study examines the thermal degradation and kinetic properties of a 1:1 eggshell-PVC (ES-PVC) mixture using thermogravimetric analysis (TGA) at different heating rates. Iso-conversional methods (FWO, KAS, Starink) were employed across  $\alpha = 0.2$ -0.8 to determine activation energies. The ES-PVC mixture exhibited a decreased DTG peak associated with HCl release, indicating suppression of autocatalytic dehydrochlorination by  $\text{CaCO}_3$ . Although its onset temperature was similar to that of pure PVC, ES-PVC showed substantially higher activation energies (302-306 kJ/mol compared to 188 kJ/mol), indicating a more stabilised and energy-intensive degradation pathway. These findings demonstrate eggshell-derived  $\text{CaCO}_3$  as an effective, sustainable co-feedstock that improves thermal resistance and offers potential for residue valorisation of the PVC.

### KEYWORD

Thermal degradation; activation energy; thermogravimetric analysis

### INTRODUCTION

The utilisation of waste-derived materials, as functional fillers in polymer systems, has gained significant attention in line with global efforts towards resource circularity and sustainable material development. Eggshell waste, generated in large quantities from domestic and industrial food processing (Baláz et al., 2019). It consists predominantly of calcium carbonate ( $\text{CaCO}_3$ ) along with a thin organic membrane, making it a low- cost inorganic-organic hybrid filler with potential value in polymer composites (Skórczewska et al., 2022). Incorporating eggshell powder into polymer matrices can reduce reliance on virgin mineral fillers while enhancing thermal, mechanical, or environmental performance (Murugan et al., 2017).

Polyvinyl chloride (PVC) remains one of the most widely used thermoplastics in construction, packaging, and consumer products. Its thermal degradation, however, proceeds through a complex multistage pathway involving an initial dehydrochlorination step followed by polyene backbone scission and char formation (Wang et al., 2016). These reactions strongly influence processing behaviour, recyclability, and end-of-life treatment. Valorising PVC with altered degradation pathways is therefore highly relevant to both material optimisation and sustainability.

Thermogravimetric analysis (TGA) provides a fundamental means of characterising polymer degradation by quantifying mass-loss transitions as temperature increases (Skórczewska et al., 2025). Complementary model-free iso-conversional kinetic methods, such as Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and Starink, enable the determination of activation energy ( $E_a$ ) without assuming a predefined reaction mechanism (Tee et al., 2025). These kinetic

approaches are widely applied to polymer-biomass and waste-derived composite systems, offering insight into the energetic and mechanistic influences of fillers on degradation behaviour.

In this context, eggshell waste presents a promising co-feedstock for valorising PVC, not only due to its  $\text{CaCO}_3$ -rich composition but also to its potential to interact chemically with chlorine-containing species released during PVC degradation. This study investigates the thermal decomposition profile and kinetic parameters of neat eggshell, neat PVC, and an eggshell-PVC mixture to assess the suitability of eggshell as a sustainable co-feedstock and to elucidate its influence on PVC degradation pathways.

## MATERIALS AND METHODOLOGY

Eggshells (ES) were collected from raw eggs and used without removal of the inner membrane to retain their natural organic content. The shells were washed with water and oven-dried at 110 °C for 24 hours. The dried fragments were milled and sieved to produce a fine powder (< 500  $\mu\text{m}$ ) before use. Polyvinyl chloride (PVC) pulverised powder from a recycling plant was used as received and dried at 60 °C for 24 hours to eliminate residual moisture. A homogeneous 1:1 wt% mixture was prepared by dry-mixing manually until uniform powder (< 500  $\mu\text{m}$ ) before use.

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 analyser. Each sample (10  $\pm$  0.1 mg) was placed in a platinum pan and heated from 30 to 950 °C under a nitrogen atmosphere (flow rate 20 mL/min) at constant heating rates of 10 and 40 °C/min. The overall thermal decomposition process involves the thermal degradation of a solid sample to produce bio-char and volatiles, which can be evaluated by the solid-state kinetic theory according to Equation (1), with the reaction rate ( $d\alpha/dt$ ) being a function of the pre-exponential factor ( $A$ ), the temperature ( $T$ ) and the conversion fraction ( $\alpha$ ):

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (1)$$

with  $\alpha = (m_o - m) / (m_o - m_f)$  and  $m$  is the mass while the terms  $o$  and  $f$  represent the initial and final mass, respectively. The term  $A$  ( $\text{s}^{-1}$ ) denotes the frequency of successful molecular collisions leading to degradation. At the same time,  $\exp(-E_a/RT)$  is the Arrhenius exponential term, where  $E_a$  (kJ/mol) is the activation energy and  $R$  is the universal gas constant (8.314 J/mol·K).

Model-free iso-conventional kinetic analysis is used to estimate the activation energy by deriving temperatures from the TG curve, corresponding to conversion levels between 0.2 and 0.8. The  $E_a$  was determined using three common models: Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and Starink. These models enable the estimation of the activation energy from the slope of the linearised plot of the logarithm of the heating rate,  $\beta$  versus temperature  $1/T$  at a constant conversion,  $\alpha$ . This process does not require the selection of any reaction model,  $g(\alpha)$ , or the reaction model function,  $f(\alpha)$ .

$$\text{FWO:} \quad \ln \beta = -1.052 \frac{E_a}{RT} + C \quad (2)$$

$$\text{KAS:} \quad \ln\left(\frac{\beta}{T^2}\right) = -\frac{E_a}{RT} + C \quad (3)$$

$$\text{Starink:} \quad \ln\left(\frac{\beta}{T^{1.92}}\right) = -1.008 \frac{E_a}{RT} + C \quad (4)$$

## RESULT AND DISCUSSION

Figure 1 shows the TGA and DTG curves of neat eggshell (ES) and PVC at heating rates of 10 and 40 °C/min. The higher heating rates shift the degradation events toward higher temperatures due to thermal lag effects (Dragan & Miclaus, 2019).

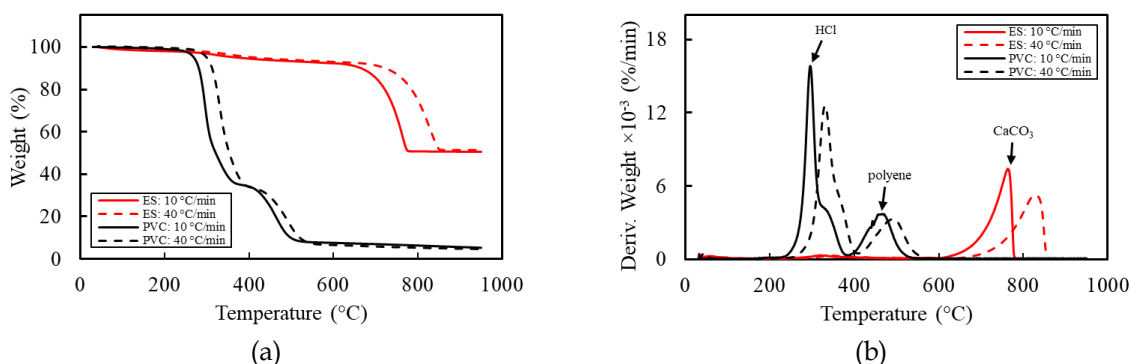


Figure 1: (a) TGA curve and (b) DTG curve for neat eggshell (ES) and PVC at 10 and 40 °C/min heating rate.

This event appears as a sharp DTG peak because dehydrochlorination is rapid and constitutes the dominant mass-loss mechanism in PVC. A secondary, broader DTG peak corresponds to the subsequent degradation of the polyene backbone formed after HCl elimination. Eggshell, in contrast, shows negligible mass loss below 600 °C. Its major decomposition event, associated with the thermal decomposition of calcium carbonate (CaCO<sub>3</sub>), occurs at 706.0 °C and 777.33 °C for heating rates of 10 and 40 °C/min, respectively.

Figure 2 illustrates the effect of incorporating eggshell into PVC on the TGA and DTG behaviours. In general, blending ES with PVC increases the residual mass by 5 times, reflecting the high thermal stability of CaCO<sub>3</sub> and its influence on the overall degradation pathway. In Figure 2(a), the ES-PVC mixture (1:1 ratio) exhibits a three-step decomposition process:

1. Initial dehydrochlorination, beginning at approximately 270.15 °C;
2. Degradation of the polyene structure at around 420.67 °C;
3. Decomposition of CaCO<sub>3</sub> in the final high-temperature stage.

This behaviour is further illustrated in Figure 2(b), where the DTG peak corresponding to HCl release is reduced in intensity compared to neat PVC, indicating an interaction between PVC and eggshell. The ES-PVC mixture exhibited noticeably lower DTG peak intensities compared to the neat samples. This reduction in mass-loss rate is attributed to the presence of CaCO<sub>3</sub> in eggshell, which reacts with and neutralises the HCl released during PVC degradation, thereby suppressing the autocatalytic dehydrochlorination pathway (Khaleghi, 2022).

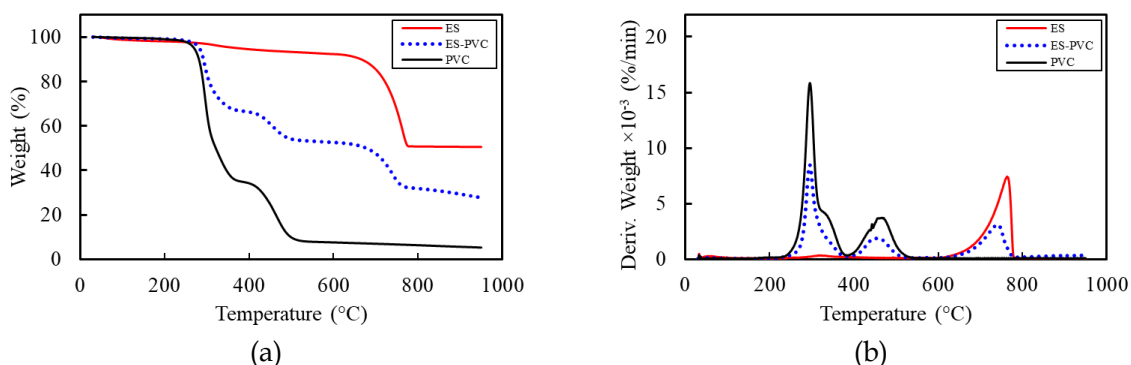


Figure 2: The changes of (a) TGA curve and (b) DTG curve for different concentration of eggshell and PVC mixture at 10 °C/min heating rate.

In addition, the formation of a thermally stable inorganic-char matrix reduces the mobility of degradation products and slows gas evolution. A dilution effect from the inorganic fraction further

contributes to the lower derivative weight loss. These combined effects result in a broader, less intense DTG profile for the mixture.

Table 1: Onset temperature, activation energy of the tested samples.

Sample	T <sub>onset</sub> (°C)		E <sub>a</sub> (kJ/mol)		
	10 (°C/min)	40 (°C/min)	FWO	KAS	Starink
ES	706.00	777.33	178.99	171.16	171.71
ES-PVC	271.83	282.17	302.33	305.80	306.05
PVC	270.50	305.33	188.12	187.80	187.78

\*Mean A is average of 10 and 40 °C/min heating rate

Table 1 summarises the onset temperature (T<sub>onset</sub>), activation energies (E<sub>a</sub>) determined using the three iso-conversional methods, and the corresponding pre-exponential factors (A) for all tested samples. The activation energy results show that the incorporation of eggshell significantly modifies the degradation pathway of PVC, leading to a substantial increase in the activation energy for the ES-PVC mixture, which ranges from 302 to 306 kJ/mol, compared to ~188 kJ/mol for neat PVC. Although the T<sub>onset</sub> of ES-PVC remains comparable to that of PVC, the elevated activation energy reflects the thermal buffering effect of CaCO<sub>3</sub> and its role as a natural stabiliser, particularly through the neutralisation of HCl during dehydrochlorination. This interaction suppresses autocatalytic degradation and enhances the ES-PVC's overall thermal resistance during its main decomposition stage.

## CONCLUSION

This study investigated the thermal degradation behaviour and kinetic characteristics of a 1:1 eggshell-polyvinyl chloride (ES-PVC) mixture using thermogravimetric analysis (TGA) at different heating rates. Model-free iso-conversional methods, Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and Starink, were applied across the conversion range  $\alpha = 0.2$ -0.8 to determine activation energies and assess the influence of eggshell-derived CaCO<sub>3</sub> on the degradation pathway. The ES-PVC mixture exhibited a notable reduction in the derivative thermogravimetric (DTG) peak intensity associated with HCl release compared to neat PVC, indicating suppression of autocatalytic dehydrochlorination due to CaCO<sub>3</sub>-HCl interactions. While the onset temperature of the mixture remained comparable to that of PVC, the activation energy increased substantially (302–306 kJ/mol vs. 188 kJ/mol), signifying a more energy-demanding and stabilised degradation pathway.

Overall, the findings demonstrate that eggshell-derived CaCO<sub>3</sub> functions not only as a sustainable co-feedstock but also as an active stabiliser that modifies PVC degradation by neutralising HCl, reducing chlorine-related emissions, lowering mass-loss rates, and enhancing thermal resistance during the main decomposition stage. Furthermore, the CaCl<sub>2</sub>-rich carbonaceous residue produced through this interaction presents opportunities for secondary valorisation, including the development of polar, surface-active hybrid materials with potential applications in niche lubrication or tribological systems, pending further material optimisation.

## ACKNOWLEDGEMENT

This work was supported by the Ministry of Higher Education (MOHE) Malaysia's Higher Institution Centre of Excellence (HICoE) program under HICoE Research Grant R.J130000.7824.4J741.

## REFERENCE

Baláž, M., Bujňáková, Z., Achimovičová, M., Tešínský, M., & Baláž, P. (2019). Simultaneous valorization of polyvinyl chloride and eggshell wastes by a semi-industrial mechanochemical approach. *Environmental Research*, 170, 332–336. <https://doi.org/10.1016/j.envres.2018.12.005>

- Dragan, S., & Miclaus, A. G. (2019). Kinetic study of sulfur dioxide absorption into dolomite-brucite suspensions. *Studia Universitatis Babes-Bolyai Chemia*, 64(2 Tom2), 345–355. <https://doi.org/10.24193/subbchem.2019.2.29>
- Khaleghi, M. (2022). Experimental and computational study of thermal behavior of PVC composites based on modified eggshell biofiller for UPVC product. *Journal of Polymer Research*, 29(1). <https://doi.org/10.1007/s10965-021-02858-7>
- Murugan, S., Munusamy, Y., & Ismail, H. (2017). Effects of chicken eggshell filler size on the processing, mechanical and thermal properties of PVC matrix composite. *Plastics, Rubber and Composites*, 46(1), 42–51. <https://doi.org/10.1080/14658011.2016.1260217>
- Skórczewska, K., Lewandowski, K., Szewczykowski, P., Wilczewski, S., Szulc, J., Stopa, P., & Nowakowska, P. (2022). Waste Eggshells as a Natural Filler for the Poly(Vinyl Chloride) Composites. *Polymers*, 14(20). <https://doi.org/10.3390/polym14204372>
- Skórczewska, K., Lewandowski, K., Wilczewski, S., Szulc, J., & Rakowska, P. (2025). Utilization of Ground Eggshell as a Biofiller of Plasticized PVC-Based Materials Fabricated Using Melt Blending. *Polymers*, 17(4). <https://doi.org/10.3390/polym17040434>
- Tee, M. Y., Wang, D., Wong, K. L., Lee, T. Z. E., Chong, W. W. F., Ng, J. H., Chong, C. T., Zakaria, Z. A., & Mong, G. R. (2025). Investigating waste valorization potential through the co-pyrolysis of waste activated sludge and polyethylene terephthalate: Analysis on thermal degradation behavior, kinetic properties and by-products. *Energy Conversion and Management*, 325. <https://doi.org/10.1016/j.enconman.2024.119412>
- Wang, M., Xia, J., Jiang, J., Li, S., Huang, K., Mao, W., & Li, M. (2016). A novel liquid Ca/Zn thermal stabilizer synthesized from tung-maleic anhydride and its effects on thermal stability and mechanical properties of PVC. *Polymer Degradation and Stability*, 133, 136–143. <https://doi.org/10.1016/j.polymdegradstab.2016.08.010>