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The Role of Calcium carboxylate in PVC Heat Stabilization: Mechanisms and Applications

Abstract

To replace heat stabilizers containing heavy metals in polyvinyl chloride (PVC), the effectiveness of calcium carboxylate synthesized from soybean wax—produced via the hydrogenation of soybean oil—as an environmentally friendly heat stabilizer was investigated. The thermal stability of PVC in the presence of this stabilizer was evaluated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA curves obtained from polymer samples indicated that decomposition occurred in two distinct stages, with the initial stage dominated by dehydrochlorination, resulting in a mass loss of more than 50%. The thermal degradation behavior was further analyzed by examining the temperatures at which the polymer mass decreased by 5%, 10%, and 20%. In the absence of a stabilizer, these temperatures were recorded as 256.56°C, 270.71°C, and 279.25°C, respectively. However, after incorporating 5 phr (parts per hundred resin) of the synthesized calcium carboxylate, the corresponding degradation temperatures increased to 270.13°C, 279.68°C, and 295.21°C, respectively. Furthermore, the activation energy of the decomposition process was determined using the Coats-Redfern integral method. The analysis revealed that the activation energy in both decomposition stages increased following the addition of the stabilizer, indicating an improvement in thermal stability. These results demonstrate that the bio-based stabilizer effectively captures hydrogen chloride (HCl) released during the thermal degradation of PVC, exhibiting a strong suppressive effect on dehydrochlorination. The findings suggest that to combine this stabilizer with other compounds may further enhance its stabilizing performance.

Keywords: *heat stabilizer, polyvinyl chloride, poly(vinyl chloride), thermal stabilizer, calcium soap, calcium carboxylate, thermal degradation*

Introduction

The increasing role of polymers in modern life is undeniable, and their potential effects on human health have raised significant concerns (Meng, Wang, Chen, 2013).

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Among the polymers that individuals encounter daily, polyvinyl chloride (PVC) is particularly notable (Wen, Yang, Yan, 2015). In terms of annual production volume, PVC ranks as the third most widely manufactured polymer, following polyethylene and polypropylene. Due to the extensive range of products made from PVC, human exposure to this polymer is substantial. PVC is a versatile, cost-effective, and durable material used in applications spanning construction materials, food packaging, artificial leather, and cable insulation (Song, Huo, Zhang, 2022; Phomin, Deberdeev, 2012).

Despite these advantages, PVC is highly susceptible to thermal degradation. Above its glass transition temperature of approximately 70°C, PVC undergoes thermal decomposition, leading to the deterioration of its physical and mechanical properties (Patrick, 2007; Yu, Sun, Ma, 2016). To mitigate this instability, heat stabilizers are commonly employed (Folarin, Sadiku, 2011). The most widely used commercial heat stabilizers include lead salts, metal soaps, organic stabilizers, and organotin compounds (Yan, Yang, 2017). However, the use of toxic heavy metal-based stabilizers, particularly lead compounds, has been restricted in developed countries and Western regions due to environmental and health concerns (Guo, Leroux, Tian, 2021). In contrast, lead-based stabilizers remain prevalent in Eastern markets, where PVC demand is highest.

In response to these regulatory and environmental challenges, extensive research is being conducted to develop effective and eco-friendly alternatives to lead-based stabilizers in PVC processing (Egbuchunam, Okieimen, Balköse, 2010). The use of metal carboxylates synthesized from vegetable oils as thermal stabilizers presents an economically viable and environmentally sustainable solution (Putrawan, Indarto, Octavia, 2022). In line with this approach, the present study investigates the thermal stabilizing effects of calcium carboxylate synthesized from partially saturated soybean wax, obtained through the hydrogenation of soybean oil. Additionally, previous research on aluminum soap derived from sunflower oil has demonstrated its potential as an effective heat stabilizer for PVC, yielding promising results (Hasanov, Mammadova, Amirov, Aliyeva, 2025).

Research

The synthesis of calcium carboxylate involved the initial saponification of soybean wax in a water-ethanol mixture using a near-stoichiometric amount of alkali, followed by the precipitation of calcium carboxylate from the resulting soap. The percentage of carboxylic acids present in the glyceride esters of soybean wax used for calcium carboxylate synthesis, along with various physicochemical properties of soybean wax, are presented in Table.

The synthesized calcium carboxylate was dried, ground into a fine powder, and mechanically blended with 5 phr of Rusvinyl PVC-S (Russia). The mixture was then subjected to a pressure of 150 bar and a temperature of 180°C using an ECOPRESS 102 (Turkey) press to produce test samples. To facilitate a comparative analysis, a control sample was prepared under identical conditions using pure PVC without any stabilizer.

Table

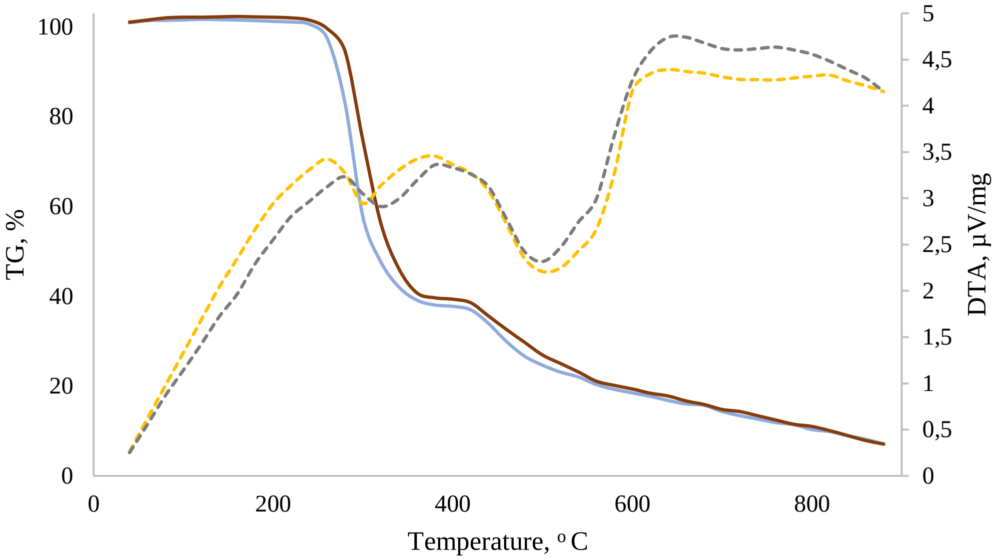
Chemical Composition and Key Analytical Parameters of Soybean Wax.

Saturated fatty acid, %	Monounsaturated fatty acid, %	Others, %	Acid value, mg KOH/g	Iodine number, g I_2/100g	Saponification value, mg KOH/g
65	30	5	0.6	30	185

The thermal behavior of the polymer samples was examined through thermogravimetric and differential thermal analysis using a NETZSCH STA449F3 Jupiter (Germany) thermogravimeter. The samples were heated up to 900°C in a nitrogen (N_2) atmosphere at a controlled heating rate of 30°C/min. The results revealed that the pure PVC sample exhibited a 5% mass loss at 256.56°C, whereas the sample containing calcium carboxylate demonstrated greater thermal resistance, with the same level of degradation occurring at 270.13°C.

Figure 1

TG and DTA curves of polymer samples.



During the initial stage of degradation, which corresponds to PVC dehydrochlorination phase, occurred mass loss with significant fluctuations, reflecting the formation of conjugated double bonds within the polymer structure. As the temperature increased, decomposition progressed more rapidly, leading to 10% and 20% mass losses at 270.71°C and 279.25°C, respectively, for the pure polymer. In contrast, the stabilized polymer sample exhibited delayed degradation, with corresponding mass losses occurring at 279.68°C and 295.21°C. These findings indicate that the incorporation of the bio-based stabilizer enhances the thermal stability of PVC.

While the pure polymer exhibited a 50% mass loss at 313.14°C, the sample containing the heat stabilizer underwent the same degree of degradation at 328.96°C, demonstrating the effectiveness of the stabilizer. The significant increase in the decomposition temperature suggests that calcium carboxylate synthesized from soy wax efficiently neutralized the HCl released from the polymer chains during the initial thermal degradation of PVC. This stabilization mechanism effectively slowed down the decomposition process, preventing the release of chlorine (Cl) atoms, which constitute the bulk of the polymer matrix. The TG-DTA curves of the polymer samples are presented in Figure 1.

According to the DTA results, energy absorption associated with the decomposition of the pure polymer occurred at lower temperatures, whereas in the sample containing the thermal stabilizer, this process was observed at higher temperatures. This shift suggests that the presence of calcium carboxylate enhances the thermal stability of PVC by delaying decomposition. Additionally, since the neutralization of the released HCl by calcium carboxylate is an exothermic process, it is possible that partial compensation of the absorbed energy occurred.

To further analyze the thermal degradation behavior, the Coats-Redfern method was employed to calculate the activation energy of the decomposition stages based on thermogravimetric data. This calculation is derived from the Arrhenius equation:

$$k(T) = Ae^{-\frac{E_a}{RT}}$$

A – Pre-exponential factor (s^{-1} or min^{-1})
E_a – Activation energy of the reaction (J/mol)
R – Universal gas constant (8.314 J/(K·mol))
T – Absolute temperature (K)

After incorporating the heating rate ($\beta = \frac{dT}{dt}$) into the Arrhenius equation, the resulting expression is:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(-\frac{E_a}{RT}\right)} f(\alpha)$$

Integrating this equation using the Coats-Redfern method yields the following expression:

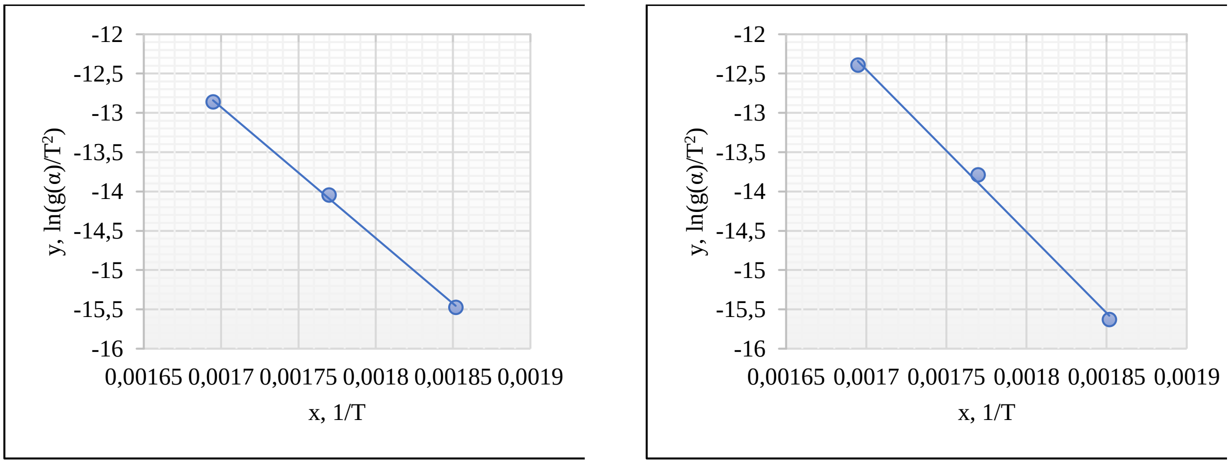
$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT}$$

The function g(α) in the equation represents the selected reaction model. For calculating the activation energy of PVC thermal decomposition using the Coats-Redfern method, three reaction models are commonly recommended:

$$\text{I. } g(\alpha) = -\ln(1-\alpha)$$
$$\text{II. } g(\alpha) = \frac{1}{(1-\alpha)} - 1$$
$$\text{III. } g(\alpha) = \left(1-(1-\alpha)^{1/3}\right)^2$$

Model I is applied to the initial stage of decomposition, specifically the dehydrochlorination process, while all three models are utilized for the second stage, where more complex chemical transformations occur.

Graphic 1.
The slopes of dehydrochlorination of PVC-pure (a) and PVC/CaSO (b) samples.



(a) (b)

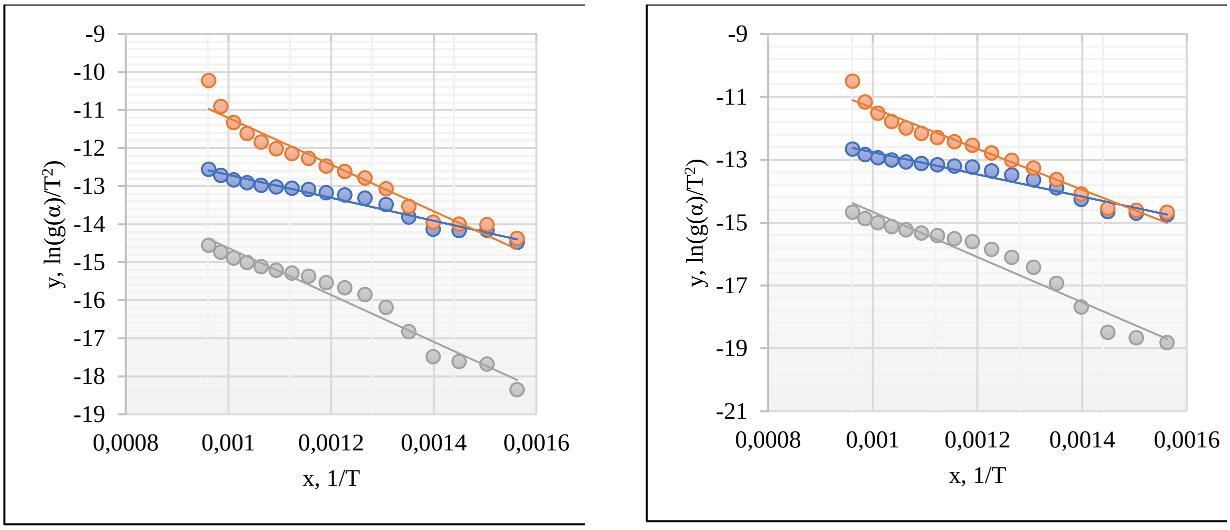
To determine the activation energy, a corresponding point for each temperature is plotted in the coordinate system y = ln(g(α)/T²) versus x = 1/T. The activation energy (E_a) is then obtained by calculating the slope of the regression line fitted to these points.

$$m = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{n\sum x^2 - \left(\sum x\right)^2}$$
$$E_a = -mR$$

m – slope

Based on the results obtained for the initial decomposition stage of the polymer samples using the aforementioned method (Graphic 1), the activation energy for the dehydrochlorination step was estimated to be approximately 62 kJ/mol for pure PVC and 65 kJ/mol for the PVC sample stabilized with a bio-based heat stabilizer. The relatively high heating rate in the thermogravimetric analysis resulted in a small difference between these values. However, the selected kinetic calculation method, which provides regression results based on a single heating rate, supports the general findings of the thermogravimetric analysis.

Graphic 2.
The slopes of polyene destruction of PVC-pure (a) and PVC/CaSO (b) samples.



(a) (b)

The results prove that the presence of the stabilizer increased the activation energy of initial decomposition stage of the polymer, indicating an improvement in thermal stability.

Following dehydrochlorination, the decomposition of the residual organic matrix occurred at a higher temperature. The degradation of the polyene structure required a greater amount of energy; however, due to the complexity of the chemical transformations occurring at this stage, the decomposition process exhibited fluctuations.

Since the degradation of the polyene structure involves complex interrelated transformations, multiple reaction models were employed to calculate the activation energy of this stage, as previously discussed. According to the calculation results (Graphic 2), the second stage of thermal decomposition exhibited a higher activation energy compared to the initial stage. Specifically, the activation energy for the second stage of thermal decomposition ranged from ≈ 83–106 kJ/mol for pure PVC and ≈ 87–110 kJ/mol for the PVC sample containing the stabilizer.

These results demonstrate that the addition of bio-derived calcium carboxylate significantly retarded the thermal decomposition of PVC. In addition to delaying the onset of polyene structure formation, the stabilizer also postponed the second stage of degradation.

Nevertheless, thermogravimetric analysis alone does not provide insight into the effects of stabilizer on other polymer properties. However, the findings indicate that calcium carboxylate synthesized from soybean wax holds promise as an effective suppressive heat stabilizer for use in the PVC processing industry.

Conclusion

The effectiveness of calcium carboxylate synthesized from soybean wax, a derivative of hydrogenated soybean oil, as an environmentally friendly heat stabilizer for polyvinyl chloride (PVC) was evaluated through thermogravimetric analysis. The results displayed that the bio-based stabilizer significantly slowed the thermal decomposition of the polymer. Notably, while the pure polymer exhibited 10% mass loss at 270.71°C, the introduction of the stabilizer increased the corresponding degradation temperature to 279.68°C. This is revealed that the HCl released during the initial decomposition of PVC was effectively neutralized by the stabilizer, thereby remaining within the total polymer mass and mitigating further degradation. Furthermore, based on the calculation of activation energies for different decomposition stages using the Coats-Redfern method, it was confirmed that calcium carboxylate positively influenced the thermal stability of PVC. However, the present study did not estimate effects of the stabilizer on other polymer properties. Despite this limitation, the thermal analysis results confirm the potential of calcium carboxylate synthesized from soybean wax as an effective suppressive heat stabilizer for PVC processing applications.

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