Eksergi
Chemical Engineering Journal
Vol 22, No. 1. 2025

ISSN: 1410-394X
e-ISSN: 2460-8203

Mix Metal Thermal Stabilizer from Palm Fatty Acid Distillate

Yona Octavia[a*], I Dewa Gede Arsa Putrawan[b]

[a]*Politeknik ATI Padang, Padang, 25171, Indonesia*

[b]*Institut Teknologi Bandung, Bandung, 40132, Indonesia*

Article history:

Submitted 20 June 2024
Revision 26 Oktober 2024
Accepted 12 November 2024
Online 5 December 2024

ABSTRACT: Polyvinyl chloride (PVC) is a widely utilized material across various fields; however, it is prone to thermal degradation, even at temperatures as low as 70°C. To enhance its thermal stability, the addition of thermal stabilizers is essential. Mixed metal stabilizers are among the most environmentally friendly and effective options, composed of carboxylate acids and a combination of alkaline earth and transition metals. This study aims to synthesize a Ca/Zn-based mixed metal stabilizer using Palm Fatty Acid Distillate (PFAD), a locally available raw material with significant potential as a source of carboxylate acid. The synthesized stabilizer, termed "Ca/Zn palmat," utilizes calcium (Ca) and zinc (Zn), chosen for their non-toxic properties. FTIR analysis confirmed the successful formation of Ca/Zn carboxylate groups from PFAD. The optimal Ca:Zn ratio was determined to be 4:1, providing a PVC stability time of approximately 15 minutes based on the Congo red test. The ideal stabilizer dosage was found to be 7 phr (parts per hundred resin). Furthermore, the addition of pentaerythritol as a co-stabilizer demonstrated a synergistic effect, significantly enhancing the thermal stability of PVC.
Keywords: PVC thermal stabilizer; palm fatty acid distillate; mix metal.

1. Introduction

Polyvinyl chloride (PVC) is a polymer composed of vinyl chloride through addition polymerization (Patrick, 2004). PVC belongs to the category of thermoplastics, which can be easily processed and shaped through heating. However, PVC is prone to degradation due to heat. Despite this drawback, its flexible/rigid nature, durability, and cost-effectiveness have made it increasingly popular. Its applications include construction materials, automotive manufacturing, medical devices, and electronics. One of the common additives added to PVC is thermal stabilizers. The function of thermal stabilizers is to prevent dehydrochlorination during heat processing, which begins to occur at temperatures around 70°C. Commonly used thermal stabilizers include lead compounds, metal mixtures, tin, and organic stabilizers. Lead stabilizers offer excellent thermal stability for PVC but are now being phased out due to their toxicity (M. Li et al., 2014).

With growing environmental awareness, the development of more eco-friendly stabilizers has become a priority. Organotin and mixed-metal thermal stabilizers are widely used because they are considered environmentally safe. The development of the PVC stabilizer industry in Asia, particularly in China, Europe, and the Americas, has been rapid due to the increasing demand for various PVC products. In Indonesia, PT Timah Industri produces tin mercaptide thermal stabilizers, and the Product Engineering Laboratory of the Bandung Institute of Technology (ITB) has also developed organotin-based stabilizers. Both tin-based stabilizers are in liquid form. However, Indonesia's PVC industry still uses lead-based stabilizers, while organotin stabilizers are less accessible due to their high cost. Moreover, liquid-phase organotin stabilizers pose a challenge for extrusion companies accustomed to using solid-phase thermal stabilizers (Arsa et al., 2022). As a result, extrusion companies prefer solid-phase mixed-metal stabilizers, which are more affordable.

Currently, mixed-metal stabilizers are imported from China. Mixed-metal thermal stabilizers are made from carboxylic acids and a mixture of bases derived from alkaline earth metals and transition metals. Indonesia has the potential to produce its own stabilizers, leveraging its abundant fatty acid resources. One of the sources of fatty acids is a byproduct of palm oil refining, known as palm fatty acid distillate (PFAD). PFAD contains over 80% free fatty acids, with palmitic acid and oleic acid as its main components. The remaining content includes triglycerides, partial glycerides, vitamin E, sterols, and volatile substances. PFAD is commonly used in the soap industry, animal feed production, and as raw material for the oleochemical industry, such as in the production of candles, cosmetics, and

* Corresponding Author: +62-82144869376
Email: yonaoctavia@poltekatipdg.ac.id

toiletries (Tay et al., 2009). Several researchers have studied the synthesis and application of mixed-metal stabilizers. M. Li et al. (2014) investigated the synthesis and testing of thermal stabilizers derived from rosin acid and dipentene. Wang et al. (2016) developed thermal stabilizers using tung-maleic anhydride (TMA) and para-aminobenzoic acid (PABA). Putrawan et al. (2022) synthesized thermal stabilizers from carboxylic acids. The methods for manufacturing thermal stabilizers were further studied by M. Li et al. (2017), comparing direct neutralization and metathesis methods using raw materials such as dimer fatty acids (DFA), maleic anhydride, and methyl eleostearate (MAME).

Beyond thermal stabilizer development, researchers have also explored co-stabilizers, such as adipic acid pentaerythritol (AAPE) combined with Ca/Zn stearate (Zhang et al., 2014), lanthanum stearate ($LaSt_3$) combined with calcium stearate and zinc glutarate (Fang et al., 2009), and zinc cyanurate synthesized from cyanuric acid and zinc acetate (S. Li and Yao, 2011). Various metal mixtures have been studied, including Ba/Zn stearate (Vymazal et al., 1983), Ba/Cd stearate (Czako et al., 1979), Na/Zn stearate (Volka et al., 1982), and Zn/Al double-layer hydroxides (Ping et al., 2006). The most commercially viable mixed-metal stabilizers are calcium and zinc-based compounds, as these metals are non-toxic. Moreover, the simultaneous use of calcium and zinc provides a synergistic effect on PVC thermal stabilization (Wang et al., 2017). A weakness of mixed-metal stabilizers is their relatively lower stabilization effectiveness compared to other types of stabilizers, such as tin-based stabilizers. This limitation is typically addressed by incorporating auxiliary co-stabilizers. One such co-stabilizer is pentaerythritol, which enhances PVC stability by forming more stable complex bonds (Liu et al., 2018).

2. Materials and Methods

This study focuses on the synthesis of mixed-metal thermal stabilizers, specifically calcium palmitate and zinc palmitate, utilizing palm fatty acid distillate (PFAD) as the source of fatty acids (palmitic acid).

2.1 Materials

The materials used for the synthesis of mixed-metal thermal stabilizers include PFAD obtained from PT Tunas Baru Lampung, as well as NaOH (Merck, 99%w), $CaCl_2$ (Merck, 99%w), $ZnSO_4$ (Merck, 99%w), and ethanol (Merck, 96%v).

2.2 Research Procedure

With the reflux apparatus set up, a specific amount of fatty acid, NaOH, and ethanol were introduced into the reactor. NaOH was added in excess (10% relative to the fatty acid). The mixture was stirred and subjected to reflux. During the reflux process, ethanol vaporized and subsequently condensed. The temperature of the water bath was maintained at 80°C to facilitate the reflux process. Reflux was carried out for 2.5 hours.

After reflux, the reaction temperature was adjusted to 75°C, and a $CaCl_2/ZnSO_4$ solution (20% excess relative to the sodium salt) was gradually added through the top of the condenser. Stirring was continued until the crystallization process was complete. The product was cooled to room temperature and filtered. The filtered product (cake) was washed with demineralized water (DM water) to separate NaCl and other impurities. Washing was repeated three times to ensure the product was free of contaminants.

The washed product was then subjected to drying under vacuum conditions (5 mmHg) at 50°C to remove residual water. The dried product was stored in a desiccator. After drying, the product was ground to obtain a powder form.

2.3 Analysis and Testing

PFAD was characterized by measuring the acid value (SNI 01-3555-1998; mg KOH/g sample), saponification value (SNI 01-3555-1998; mg KOH/g sample), iodine value (SNI 01-3555-1998; g iodine/100 g sample), unsaponifiable matter, moisture content, and titer (AOAC Official Method; °C). The mixed-metal stabilizers were characterized using FTIR to confirm the functional groups present. Thermal stability testing was conducted, including a static Congo red test.

3. Results and Discussion

3.1. Characteristics of Fatty Acids

PFAD is utilized as a source of fatty acids (palmitic acid) for the production of calcium palmitate and zinc palmitate. The characterization of PFAD was conducted by measuring the acid value, saponification value, iodine value, titer, moisture content, and unsaponifiable matter. The results are presented in Table 1.

Table 1. Characteristics of PFAD

Measurement	Value
Acid value (mg KOH/g)	193.08 ± 0.40
Saponification value (mg KOH/g)	205.31 ± 1.04
Iodine value (g I_2/100 g)	56.05 ± 1.01
Titer (°C)	45.12 ± 0.57
Moisture content (%)	0.78 ± 1.07
Unsapified fraction (%)	1.60 ± 0.50

The molecular weight of PFAD was calculated as 267.03 g/mol based on the acid value, saponification value, moisture content, and unsaponifiable matter. The high acid value indicates a significant content of free fatty acids, while the higher saponification value suggests the presence of triglycerides in PFAD. The iodine value reflects the degree of unsaturation in the fatty acids. PFAD contains nearly equal proportions of saturated and unsaturated fatty acids, dominated by 46.9% palmitic acid and 4.3% stearic acid as saturated components, and 36.7% oleic acid and 9.03% linoleic acid as unsaturated components (Tay et al., 2009).
The solidification temperature of PFAD is 45°C, rendering it solid at room temperature. Figure 1 shows the IR spectra of PFAD and the synthesized Ca/Zn palmitate stabilizers. The characteristics of PFAD as a source of palmitic acid are indicated by the IR peak at 1707 cm^{-1}, representing the C=O functional group. The broad O-H absorption band between

ISSN: 1410-394X
e-ISSN: 2460-8203

2400–3400 cm^{-1} and the combination of C=O and O-H absorption are key indicators of carboxylic acid groups in the FTIR spectrum. The peak at 3000 cm^{-1} indicates the presence of C=C-H double bonds, confirming the unsaturated nature of the fatty acids.

3.2. Characteristics of the Product

The synthesis of Ca/Zn palmitate stabilizers was conducted in duplicate, producing two products named Ca/Zn Palmitate I and II, both of which were characterized using FTIR analysis.

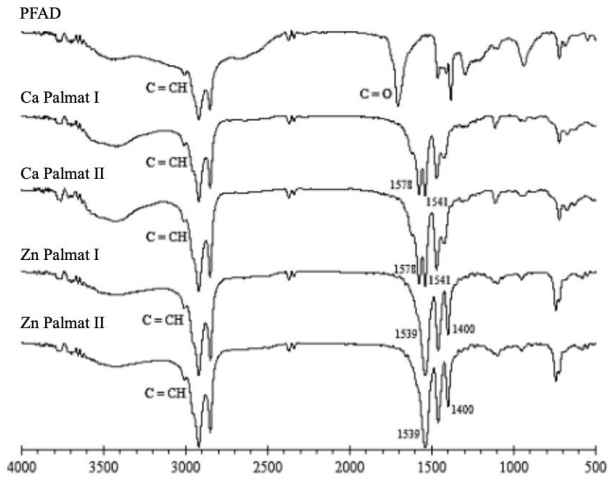

Figure 1. FTIR PFAD , Ca Palmat I, Ca Palmat II, Zn Palmat I dan Zn Palmat II

The peak frequency of DALS at 1707 cm-1, which indicates the C=O group, shows a different shape compared to the peak of the product. This suggests a bond change in the reaction, indicating the formation of calcium palmitate or zinc palmitate. According to Gonen et al. (2010), the characteristic peaks of calcium palmitate are at frequencies of 1542 cm-1 and 1575 cm-1. These peaks are formed due to the asymmetric stretching of monodentate and bidentate with calcium ions. In this study, the IR spectra measurements for both calcium palmitate I and calcium palmitate II are characterized by peaks at frequencies of 1578 cm-1 and 1541 cm-1. As for the characteristics of zinc palmitate, according to Gonen et al. (2005), they are found at frequency peaks of 1540 cm-1 and 1398 cm-1. These characteristics were also measured in this study for both zinc palmitate I and zinc palmitate II at frequency peaks of 1539 cm-1 and 1400 cm-1.

3.3. Thermal Effectiveness of the Stabilizer

The thermal effectiveness of the stabilizer was assessed based on its ability to resist PVC degradation. Degradation releases hydrogen chloride (HCl), which discolors PVC and acts as a catalyst for further degradation, forming polyene chains. Thus, HCl release is a key indicator of thermal stability. A static Congo red test was used to evaluate stability.

3.4. Effect of Ca/Zn Ratio on Thermal Effectiveness

The roles of calcium and zinc palmitate differ in inhibiting degradation. Zinc palmitate acts as a primary stabilizer, while calcium palmitate serves as a secondary stabilizer. The Ca/Zn ratio is critical to optimizing performance. Ratios of 1:4, 1:1, 4:1, and 7:1 were evaluated, with results presented in Figure 2.

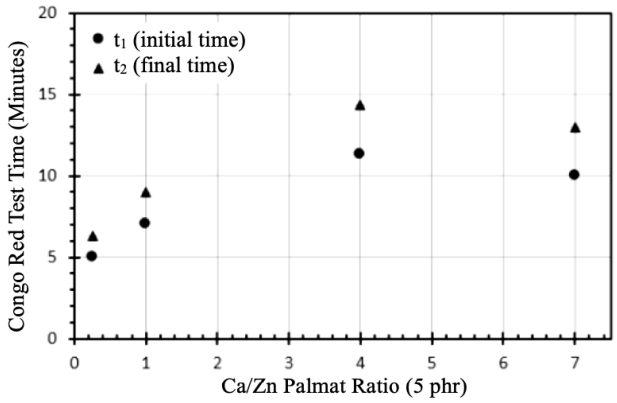

Figure 2. Influence of Ca/Zn Ratio on Congo Red Stability Test

Zinc palmitate functions to provide short-term stability by replacing allylic chlorine or tertiary chlorine on PVC with a carboxylate group, and then zinc will bind chloride to form zinc chloride. Zinc chloride is a Lewis acid that can bind more than two chloride atoms, making it a catalyst in the degradation of PVC. This process is often referred to as "zinc burning." The autocatalytic reaction that occurs leads to poor long-term stability when using only zinc palmitate as a stabilizer. Therefore, calcium palmitate is added to regenerate zinc chloride, thus inhibiting the reaction of zinc chloride with other chloride atoms.

Based on this reaction mechanism, it can be concluded that adding a higher ratio of calcium palmitate compared to zinc palmitate in the correct ratio can prevent zinc burning, thereby improving the long-term stability of PVC. If zinc burning is inhibited, the degradation rate of PVC becomes slower. The most effective ratio in this study is 4:1, which is in line with the results of Balkose et al. (2001), providing stability of t1 = 11.33 minutes and t2 = 14.33 minutes.

3.5. Effect of Stabilizer Dose (phr) on Thermal Effectiveness

Congo red tests were conducted at the optimal Ca/Zn ratio of 4:1 with stabilizer doses of 1, 3, 5, 7, and 10 phr, as shown in Figure 3. The Congo red test demonstrated that the increase in stabilizer dose (phr) of Ca/Zn palmitate is not linear with respect to PVC stability. PVC stability gradually improved from a stabilizer dose of 1 phr and showed a significant increase at 7 phr; however, at 10 phr, stability decreased. While higher stabilizer doses introduce more

compounds that mitigate the degradation rate, the presence of the stabilizer itself can trigger autocatalytic reactions.

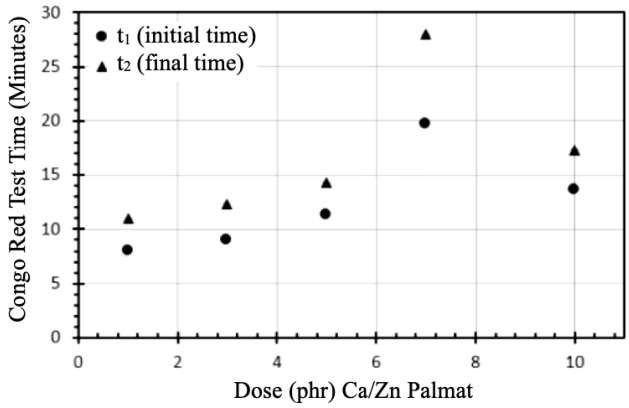

Figure 3. Effect of Stabilizer Dose (phr) on Congo Red Stability Test

The autocatalytic reaction of zinc chloride, originating from zinc palmitate stabilizer, can accelerate the degradation rate due to the increased release of hydrogen chloride. Furthermore, the hydrogen chloride produced can degrade calcium palmitate into carboxylic acid and calcium chloride, rendering it ineffective in regenerating zinc chloride. This autocatalytic reaction, caused by the stabilizer, reduces PVC stability, making the stabilizer less effective. Thus, higher stabilizer doses (phr) do not always enhance stabilizer effectiveness.

An optimal stabilizer dose (phr) that effectively suppresses PVC degradation must be determined. In this study, a dose of 7 phr with a Ca/Zn ratio of 4:1 was found to meet the practical requirements for PVC extrusion, providing stability times of t_1 = 20 minutes and t_2 = 28 minutes. The stabilizer dose added to PVC should be minimal while effectively inhibiting dehydrochlorination. In practical applications, a 7 phr dose of stabilizer is relatively high but still acceptable. The stabilizer's effectiveness can be further enhanced by incorporating co-stabilizers.

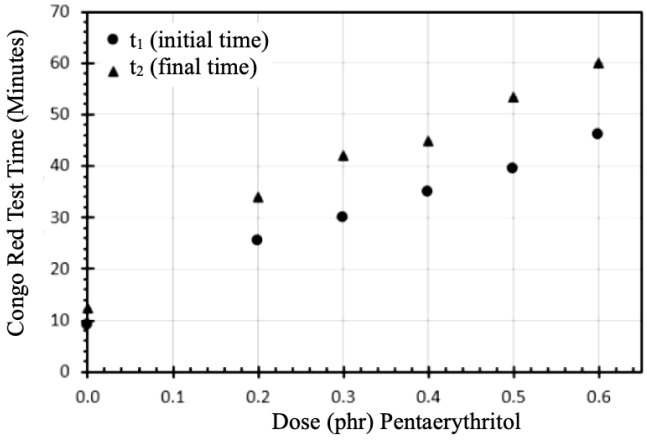

Figure 4. Effect of Pentaerythritol Dose on Ca/Zn Palmitate Stabilizer Effectiveness

3.6. Effect of Co-Stabilizer on Thermal Effectiveness

In this study, the co-stabilizer used was pentaerythritol. The commonly used industrial dosage of the co-stabilizer ranges between 0.2–0.6 phr. Therefore, the dosage (phr) of pentaerythritol was varied at a Ca/Zn palmitate ratio of 4:1 with six different doses of 3 phr. The effect of pentaerythritol dosage (phr) based on the Congo red test is shown in Figure 4. As the pentaerythritol dosage (phr) increases, the stability of PVC also improves. The addition of the co-stabilizer extended the stability time to t_1 = 45 minutes and t_2 = 60 minutes.

4. Conclusions

Based on the discussions and analysis that have been carried out, it can be concluded that the thermal stabilizer for PVC based on a metal mixture (Ca/Zn) can be synthesized from Palm Fatty Acid Distillate (PFAD), with the effective Ca/Zn palmitate ratio being 4:1 and the most effective usage dose being 7 phr. Pentaerythritol provides a synergistic effect as a co-stabilizer in the Ca/Zn palmitate stabilizer mixture at a 4:1 ratio and a dose of 3 phr.

Acknowledgements

The author would like to thank PT. Tunas Baru Lampung and PT Timah Indonesia for their assistance with the raw materials for the experiment.

Statement

During the preparation of this work the authors used ChatGPT 4 and Grammarly in order to improve English language and proofread the text. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

CRediT authorship contribution statement

Yona Octavia: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis.
I Dewa Gede Arsa Putrawan: Validation, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential**.**

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