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COLORIMETRIC STUDY OF MUTUAL SYNERGETICS OF BIO-BASED PVC THERMAL STABILIZERS

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Colorimetric analysis was employed to determine whether a synergistic effect occurs when calcium and aluminum carboxylates synthesized as thermal stabilizers are used in combination to enhance the thermal stability of polyvinyl chloride (PVC)-based composite materials. For comparative evaluation, a commercial NV-brand Ca/Zn stearate-based thermal stabilizer was used as a reference. The results indicated that both bio-based thermal stabilizers improved the long-term thermal stability of the polymer; however, they did not exert a significant influence on the initial color characteristics. The chemical compatibility of the thermal stabilizers with PVC was evaluated by assessing the flow behavior of the melt blends. The findings demonstrated a high degree of compatibility between aluminum carboxylate and PVC, whereas the commercial thermal stabilizer led to phase separation.

Keywords: *PVC, thermal stabilizer, initial whiteness, green additive, colorimetry*

INTRODUCTION

Since the second half of the twentieth century, the widespread use of polymers and polymer-based composite materials in various industrial sectors, as well as in everyday life, has led to a rapid increase in their production volumes. This growth has, in turn, given rise to significant scientific, technical, environmental, and economic challenges associated with the additives used during polymer processing, including stabilizers, plasticizers, fillers, and other functional additives. The selection of appropriate additives, particularly for polymers subjected to thermal processing, has a direct and critical impact on the performance and service properties of the resulting materials [1-3]. Among the plastic materials most widely used in daily applications are those based on polyvinyl chloride (PVC). Despite its broad range of applications, one of the principal drawbacks of PVC is its inherent thermal instability. Under elevated temperatures, PVC readily undergoes dehydrochlorination, leading to the release of hydrogen chloride, discoloration of the material, and a pronounced deterioration of its mechanical properties. For this reason, the industrial production and processing of PVC-based materials have become feasible only through the use of thermal stabilizers [4-8].

Over the past decades, extensive research efforts have been devoted to addressing this limitation, and numerous thermal stabilizer systems based on metal soaps, complex compounds, and organic-inorganic hybrid systems have been synthesized and evaluated. Although high stabilization efficiency has been achieved in some cases, the widespread industrial application of many of these systems has been restricted by their high cost, toxicity, and adverse environmental impact. In particular, the environmental and health risks associated with lead-based and certain heavy-metal stabilizers have necessitated the development of safer and more sustainable alternatives [9-12].

In response to these challenges, increasing attention has recently been directed toward the use of bio-based raw materials. Both by-products and primary products of industries utilizing plant-derived feedstocks have been investigated for this purpose, with promising results reported in several studies. The key advantages of bio-based raw materials include their renewable nature, relatively low cost, reduced toxicity, and improved environmental compatibility. Moreover, derivatives obtained from bio-based substances often exhibit good compatibility with polymer matrices, further enhancing their potential for practical applications [13-17]. In this context, vegetable oils—particularly sunflower oil, which is an abundant and readily available resource—have attracted considerable interest. Metal carboxylates synthesized from the fatty acids of sunflower oil have emerged as promising candidates for use as thermal stabilizers for PVC. Among them, calcium and aluminum carboxylates exhibit significant potential due to their stabilizing capability and favorable interaction with the polymer matrix. The bio-based origin of these compounds further enhances their attractiveness from both environmental and economic perspectives.

Therefore, the investigation of sunflower oil-based calcium and aluminum carboxylates as thermal stabilizers for PVC is of considerable scientific and practical significance, contributing to the development of new stabilization systems that are environmentally benign, economically viable, and derived from renewable raw materials as alternatives to conventional industrial stabilizers.

EXPERIMENTAL PART

Materials

For the synthesis of metal carboxylates, sunflower oil (Final grade), potassium hydroxide (KOH, Lacherma), calcium chloride ($CaCl_2$, Vekton), and aluminum sulfate octadecahydrate ($Al_2(SO_4)_3 \cdot 18H_2O$, Kimyalab) were used as received.

For the preparation of PVC samples, polyvinyl chloride (PVC, Rusvinyl PVC-S grade), dibutyl phthalate (Vekton), a commercial Ca/Zn stearate-based thermal stabilizer (NV), and titanium dioxide (TiO_2, Kronos) were employed.

Methods

The synthesis of metal carboxylates was carried out using established scientific procedures. Initially, sunflower oil was saponified with an alkali in a water-alcohol medium, followed by precipitation of the resulting water-soluble soap with calcium and aluminum salts. The obtained metal carboxylates were thoroughly washed and dried to constant mass [18,19].

PVC samples were prepared using various formulations. To evaluate the compatibility of PVC/thermal stabilizer mixtures by optical microscopy, thermal stabilizers were incorporated into the polymer at a concentration of 5 phr, and binary mixtures were prepared. For melt flow index (MFI) measurements, an additional 20 phr of dibutyl phthalate was introduced as a plasticizer. To assess the influence of thermal stabilizers on the color properties of PVC by colorimetric analysis, 5 phr of TiO_2 was added to the binary mixtures. For investigation of the synergistic effect between calcium and aluminum carboxylates, Ca/Al carboxylate mixtures were prepared at mass ratios of 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100, with a total stabilizer content fixed at 5 phr.

PVC samples were prepared using a heated press (ECOPRESS 103, Turkey). Pressing was performed at a temperature of 180 °C under a pressure of 150 bar. For microscopic observations and MFI measurements, samples were held under these conditions for 40 s, whereas for colorimetric measurements, pressing times of 40, 120, 240, 360, and 480 s were applied.

Optical microscopy was conducted using an Olympus BX53M microscope. Melt flow index measurements were performed using an XNR-400 MFI tester at 180 °C under a load of 12.59 kg, and colorimetric analyses were carried out with a HunterLab MiniScan portable colorimeter.

RESULTS AND DISCUSSION

The properties of the synthesized metal soaps varied depending on the incorporated metal ion. Calcium carboxylate (CaSUN) was obtained as a white to yellowish powder, whereas aluminum carboxylate (AlSUN) was formed as a transparent, orange, gel-like material. Although calcium carboxylate exhibits hygroscopic behavior, aluminum carboxylate was selected due to its hydrophobic nature. The physicochemical properties of CaSUN showed notable similarities to those of the commercial thermal stabilizer NV, which was therefore chosen as a reference material. To assess the compatibility of the thermal stabilizers with the polymer matrix, optical microscopy images of the prepared PVC-based samples are presented in Figure 1. Specifically, Figure 1A and 1B correspond to PVC/CaSUN compositions at ratios of 100/3 and 100/5, respectively, while Figure 1C and 1D show PVC/AlSUN samples at the same loadings. Figure 1E depicts the PVC/NV (100/5) system. The micrographs of hybrid stabilizer systems, PVC/Ca-AlSUN (100/5), with Ca:Al ratios of 3:1, 4:1, and 5:1 are presented in Figure 1F, 1G, and 1H, respectively.

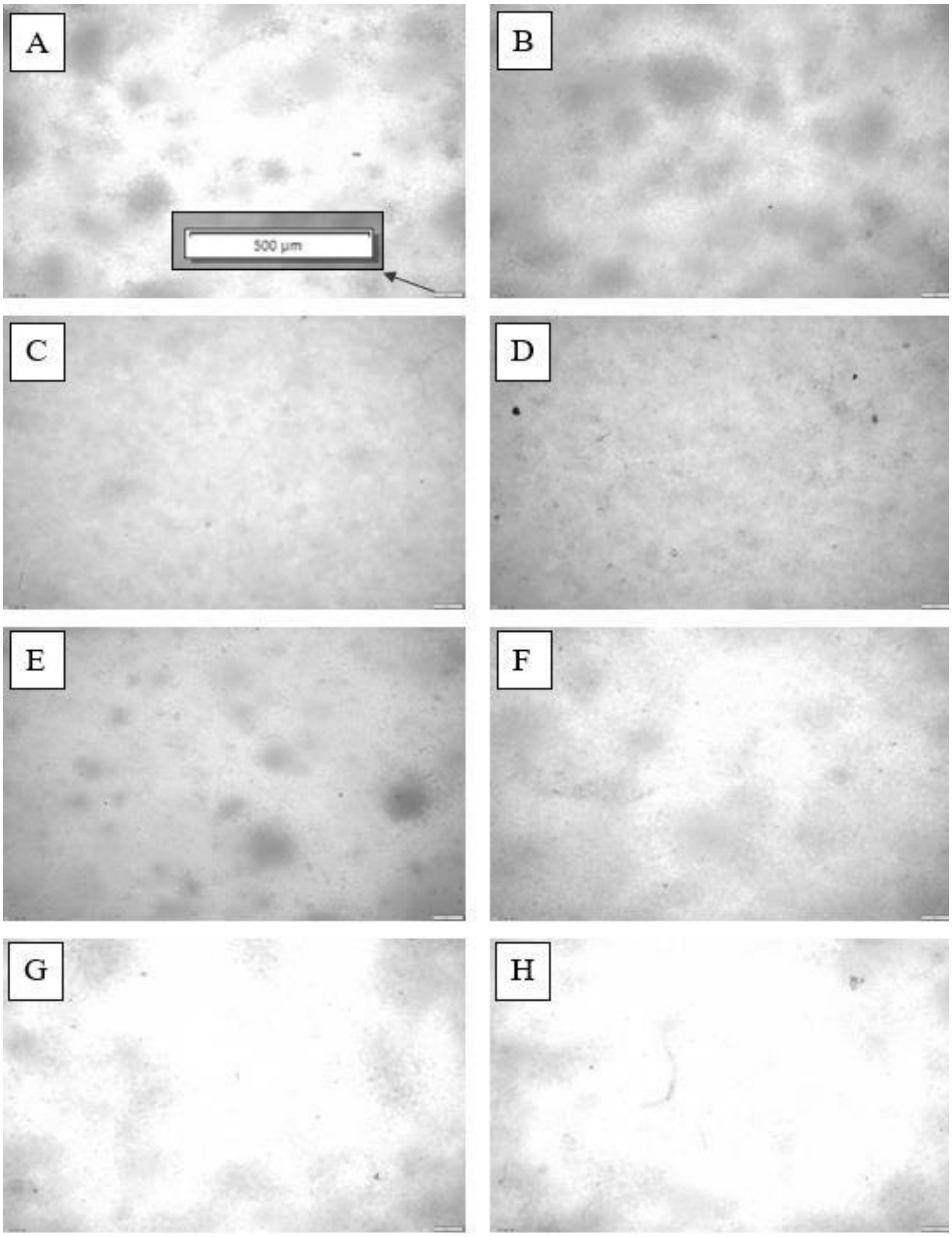

Fig.1. Microscopic pictures of PVC/thermal stabilizer samples

As observed in the micrographs, increasing the content of SUN-based carboxylates to 100/5 leads to a more complex microstructure. Under these conditions, the formation of local agglomerated regions becomes possible; however, these agglomerates do not behave as rigid or hard phases. Instead, they appear as soft, diffuse domains, which can be attributed to the high segmental mobility of the unsaturated aliphatic chains. Consequently, the system maintains an overall elastic and structurally adaptable character. This type of morphology indicates that the metal carboxylates interact with the PVC matrix predominantly through strong physical-molecular interactions rather than through chemical bonding. Distinct morphological differences were identified between CaSUN- and AlSUN-based systems. In Al-based carboxylates, the interfacial interactions are comparatively more rigid due to the higher valence state of the aluminum ion, resulting in a denser and more compact microstructure in certain regions. In contrast, Ca-based systems exhibit a softer and more elastic morphology. A similar structural appearance is also observed in the PVC/NV sample. In the case of the commercial thermal stabilizer, the presence of mineral components contributes to the formation of local inhomogeneous regions; however, the absence of sharp boundaries indicates good interfacial compatibility with the polymer matrix.

When CaSUN and AlSUN are simultaneously incorporated into PVC at a total loading of 5 phr but at different ratios (3:1, 4:1, and 5:1), the optical properties of the resulting composites vary depending on the metal carboxylate ratio. A decrease in the AlSUN content leads to an increase in sample transmittance. This behavior suggests that Al^{3+} ions are capable of forming cross-coordination interactions between polymer chains, which enhance light scattering and reduce optical transparency. Similar trends are reflected in the MFI results of PVC-based compositions presented in Figure 2. Although the incorporation of 20 phr DBF plasticizer improves polymer flowability to some extent, the results clearly demonstrate that the type of thermal stabilizer is the dominant factor governing the melt flow behavior of the blends.

The PVC/DBF system exhibited the lowest MFI value among all samples, indicating limited melt flowability. In contrast, the PVC/NV/DBF composition showed the highest melt flow rate, which can be attributed to a pronounced layering effect. This suggests that NV effectively reduces internal friction within the polymer matrix, thereby facilitating melt flow. For the PVC/DBF/CaSUN system, the MFI values were comparable to those obtained using the commercial thermal stabilizer, indicating similarly high melt flowability. Conversely, a significant reduction in MFI was observed for the PVC/DBF/AlSUN sample. This behavior can be explained by the stronger interaction between AlSUN and PVC chains, leading to increased molecular entanglement and restricted melt flow. Such structural characteristics are generally favorable for enhancing the mechanical performance of the composite.

Overall, the MFI results confirm that the melt flow behavior of PVC-based compositions is primarily determined by the chemical nature of the stabilizer. This, in turn, has a direct impact on the processability and final performance characteristics of the material.

Figure 3 illustrates the time-dependent variation of the whiteness index (L* value, CIE Lab color space) of PVC/TiO_2 composite samples containing different thermal stabilizers, measured at 180 °C. For all samples, a gradual decrease in the L* value with increasing exposure time was observed, which is indicative of progressive discoloration caused by PVC dehydrochlorination during thermal processing.

The most pronounced loss of whiteness was recorded for the unstabilized PVC/TiO_2 sample. In this case, the L* value decreased from approximately 92 at 40 s to about 73-74 at 480 s, demonstrating the poor color stability of PVC in the absence of a thermal stabilizer and confirming the accelerated nature of thermal degradation under these conditions.

In contrast, the use of a commercial Ca/Zn stearate-based thermal stabilizer (PVC/NV/TiO_2) resulted in the highest preservation of whiteness throughout the test duration. Even after 480 s, the L* value remained close to 90, highlighting the high efficiency of the Ca/Zn stabilizer system in maintaining the original color of PVC during thermal exposure.

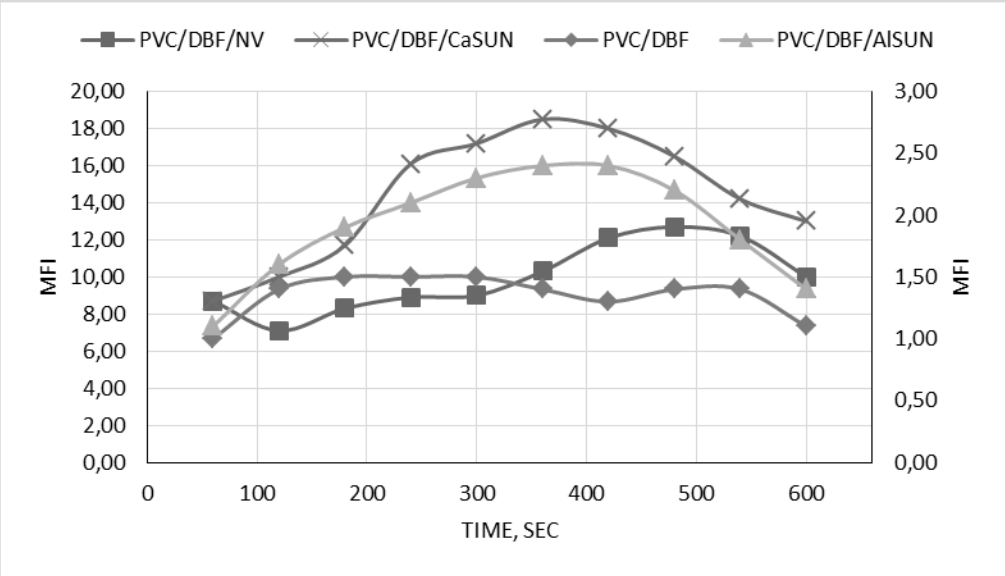

Fig.2. MFI curves of PVC samples

The PVC/CaSUN/TiO_2 sample stabilized with bio-derived calcium carboxylate exhibited improved color stability compared to the unstabilized system; however, a noticeable decline in the L* value was still observed with increasing time. This suggests that while calcium carboxylate contributes positively to the long-term thermal stabilization of PVC, its ability to preserve the initial whiteness is limited. A comparatively better performance was observed for the aluminum carboxylate-stabilized sample (PVC/AlSUN/TiO_2). At the end of the 480 s exposure, the L* value remained at approximately 82, indicating enhanced color retention relative to the CaSUN-stabilized system. This behavior suggests improved chemical compatibility and more effective inhibition of discoloration in the presence of aluminum carboxylate.

Overall, the results demonstrate that bio-derived calcium and aluminum carboxylates enhance the thermal stability of PVC, although their effectiveness in maintaining the initial color properties remains inferior to that of the commercial Ca/Zn stabilizer. Among the bio-based stabilizers, aluminum carboxylate provides superior colorimetric stability compared to calcium carboxylate. Furthermore, previous thermogravimetric investigation showed that the onset of mass loss for PVC stabilized with AlSUN occurred at higher temperatures than for the other samples, indicating a more complex stabilization mechanism [20]. Although AlSUN is less effective in preserving the initial color compared to the commercial stabilizer, it offers improved long-term thermal stability.

The synergistic effect observed when multiple thermal stabilizer components are employed within a single system arises from the attainment of an overall thermal stability that exceeds the contribution of each individual component. Consequently, commercial thermal stabilizer formulations are typically complex and consist of combinations of components designed to complement one another. In conventional systems, zinc stearate is effective in providing high initial whiteness and favorable visual appearance; however, under elevated temperatures and prolonged processing conditions, it promotes rapid discoloration and material degradation due to the formation of autocatalytic decomposition products such as $ZnCl_2$. In contrast, calcium stearate enhances long-term thermal stability through its ability to scavenge HCl, although it is comparatively less effective in maintaining initial whiteness.

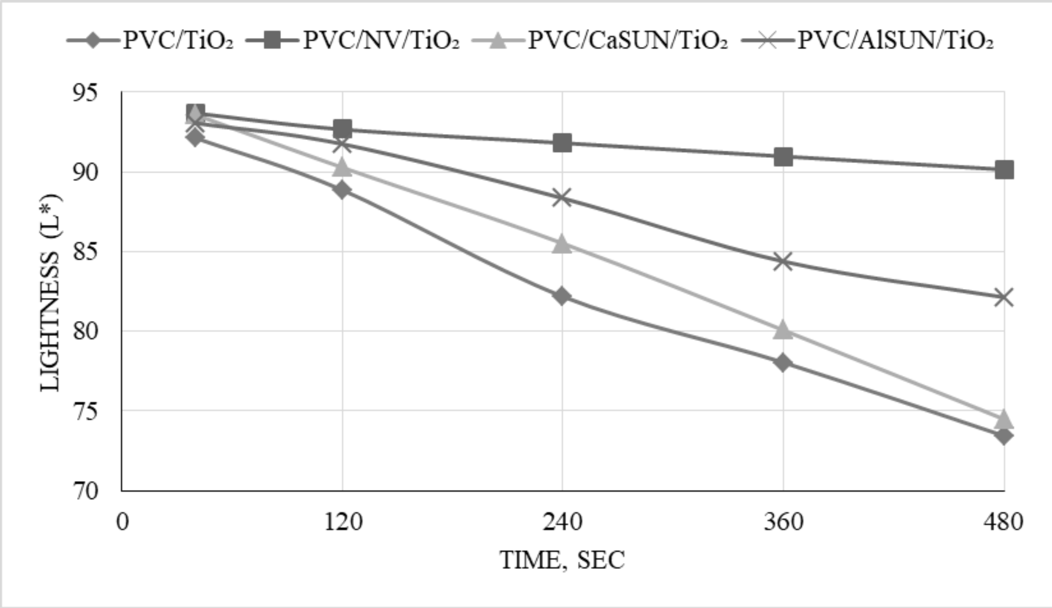

Fig.3. Lightness (L*) Changes of PVC/TiO_2-Based Composites Over Time

To address these limitations, the combined use of bio-derived metal carboxylates in varying ratios was investigated using colorimetric analysis. As illustrated in Figure 4, whiteness and color change parameters measured for different formulations were systematically compared. Among the evaluated systems, the results obtained for Ca-Al carboxylate mixtures are particularly noteworthy.

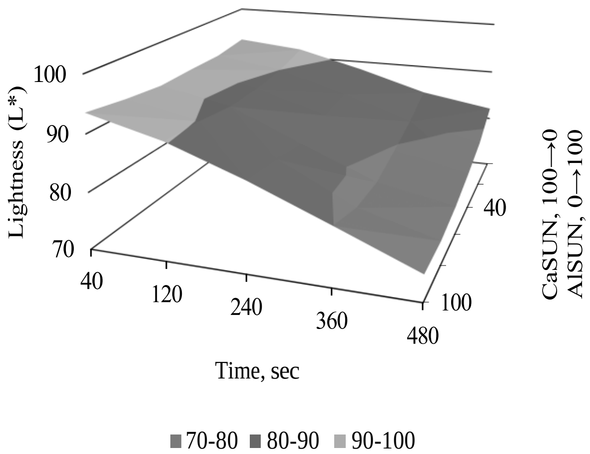

Fig.4. Effect of CaSUN/AlSUN ratio on color stability of PVC/TiO_2 formulations

The data presented in Figure 4 demonstrate a clear trend of improved color retention with increasing Al carboxylate content. This improvement follows a predominantly static behavior, indicating the absence of a pronounced synergistic interaction between the metal carboxylates. In other words, the enhanced color stability can be attributed primarily to the increasing proportion of Al carboxylate rather than to cooperative effects between the stabilizer components. Accordingly, higher Al carboxylate concentrations result in better preservation of initial whiteness and a reduced extent of color change during thermal exposure. These findings suggest that there is no significant interaction among CaSUN, AlSUN, or their intermediate species under the investigated conditions, and that the observed stabilization effect is governed mainly by the intrinsic contribution of the Al-based carboxylate.

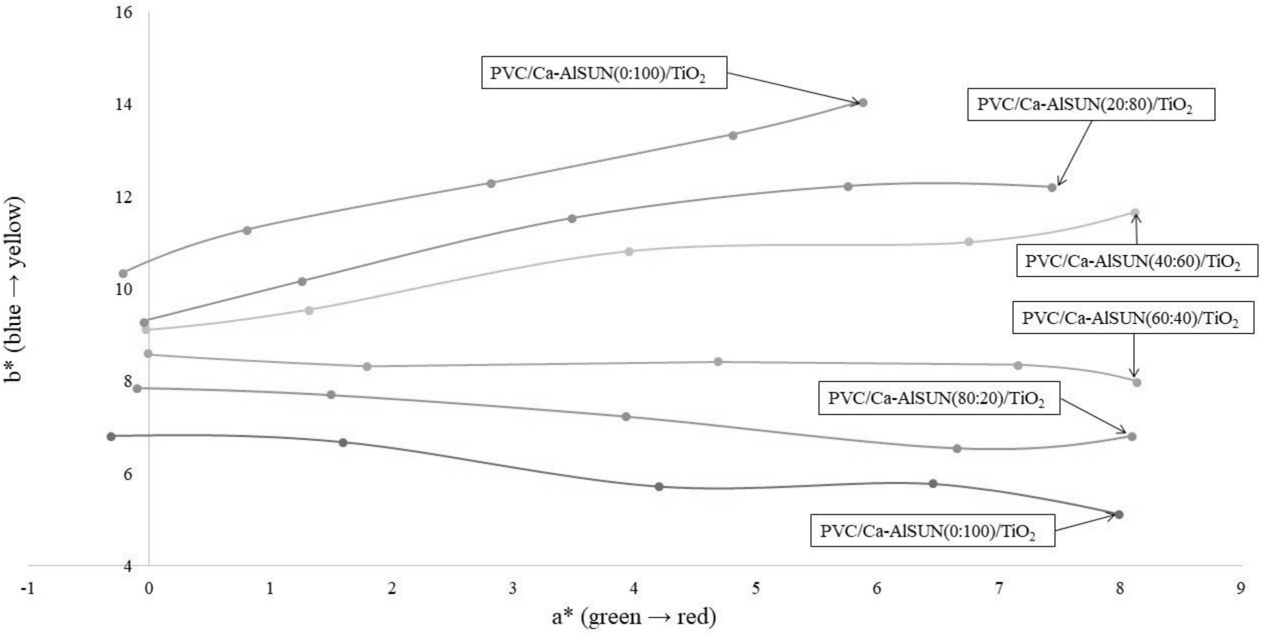

Fig.5. Color cordinate of PVC/Termal stabilizer/TiO_2 samples

The absence of a synergistic effect is also observed in the a*–b* color coordinate system (Figure 5). With increasing AlSUN content, redness is progressively replaced by yellowness, and the most pronounced effect is obtained for the PVC/AlSUN/TiO_2 sample.

CONCLUSION

This study investigated the mutual synergistic behavior of bio-based calcium and aluminum carboxylates derived from sunflower oil as thermal stabilizers for PVC. The results show that both CaSUN and AlSUN improve the thermal stability of PVC, with aluminum carboxylate exhibiting better compatibility with the polymer matrix and superior long-term color stability compared to calcium carboxylate. Optical microscopy and melt flow index analyses confirmed stronger interactions between AlSUN and PVC, which contribute to its stabilizing performance. Colorimetric measurements revealed that increasing the AlSUN content in CaSUN–AlSUN mixtures leads to improved preservation of whiteness and reduced color change during thermal exposure. However, this improvement follows a static trend, indicating that the observed enhancement is mainly due to the intrinsic stabilizing effect of AlSUN rather than a true synergistic interaction between the stabilizers. This conclusion is further supported by the a*-b* color coordinate analysis, which shows a gradual shift from red to yellow tones with increasing AlSUN content, with the most stable color characteristics observed for the PVC/AlSUN/TiO_2 system.

Overall, the findings suggest that sunflower oil–based aluminum carboxylate is a promising environmentally friendly thermal stabilizer for PVC, offering improved long-term thermal stability and acceptable color performance. Although no synergistic effect was detected in CaSUN–AlSUN combinations, the results provide valuable guidance for the development of sustainable PVC stabilization systems based on bio-derived additives.

REFERENCES

1. Lewandowski, K., Skórczewska, K.A. Brief review of poly (vinyl chloride) (PVC) recycling // Polymers. – 2022, 14, – p. 3035.
2. Xu, J. Separation of copper and polyvinyl chloride from thin waste electric cables: A combined PVC-swelling and centrifugal approach / J. Xu., S. Kumagai., T. Kameda [et al.] // Waste Management, – 2019, 89, – p. 27–36.
3. Annual production of polymer resin and fibers (Sep. 2023) // Our World in Data. – https://ourworldindata.org/grapher/global-plastics-production
4. Jia L., Yin L., Luo Z. et al. Molecular chain model construction, thermo-stability, and thermo-oxidative degradation mechanism of poly (vinyl chloride) / L. Jia., L. Yin., Z. Luo [et al.] // RSC Advances, – 2016, 6, – p. 31898–31905.
5. Pandey M., Joshi G.M., Mukherjee A. et al. Electrical properties and thermal degradation of poly(vinyl chloride)/polyvinylidene fluoride/ZnO polymer nanocomposites / M. Pandey., G.M. Joshi., A. Mukherjee [et al.] // Polymer International, – 2016, 65 (9), – p. 1098–1106.
6. Rijavec T., Strlič M., Cigić I.K. Plastics in heritage collections: poly (vinyl chloride) degradation and characterization // Acta Chimica Slovenica, – 2020, 67. – p. 993–1013.
7. Tahira B.E., Khan M.I., Saeed R. A review: Thermal degradation and stabilization of poly (vinyl chloride) / B.E. Tahira., M.I.Khan., R. Saeed [et al.] // International Journal of Research, – 2014, 1 (6), – p. 732–750.
8. Wang Z., Xie T., Ning X. Thermal degradation kinetic study of polyvinyl chloride (PVC) sheath for new and aged cables / Z. Wang., T. Xie., X. Ning [et al.] // Waste Management, – 2019, 99, – p. 146–153.
9. Yousif E., Salimon J., Salih N. New stabilizers for PVC based on some diorganotin(IV) complexes with benzamidoleucine / E. Yousif., J. Salimon., N. Salih [et al.] // Arabian Journal of Chemistry, – 2016, 9 (2), – p. S1394–S1401.
10. Ahmed D.S., Kadhom M., Hadi A.G. Tetra Schiff bases as polyvinyl chloride thermal stabilizers / D.S. Ahmed., M. Kadhom., A.G. Hadi [et al.] // Chemistry, – 2021, 3 (1), – p. 288–295.
11. Akram E., Rashad A., Ali M. Ionic liquids: A new generation of efficient polyvinyl chloride thermal stabilizers / E. Akram., A. Rashad., M. Ali [et al.] // Journal of Umm Al-Qura University for Applied Sciences, – 2024, 10, – p. 12–19.
12. Asawakosinchai A., Jubsilp C., Mora P. Organic heat stabilizers for polyvinyl chloride (PVC): A synergistic behavior of eugenol and uracil derivative / A. Asawakosinchai., C. Jubsilp., P. Mora [et al.] // Journal of Materials Engineering and Performance, – 2017, 26 (10), – p. 4781–4788.
13. Bouchoul B., Benaniba M.T., Massardier V. Thermal and mechanical properties of bio-based plasticizers mixtures on poly (vinyl chloride) // Polimeros, – 2017, 27 (3), – p. 237–246.
14. Ye Q., Ma X., Li B. Development and investigation of lanthanum sulfadiazine with calcium stearate and epoxidised soybean oil as complex thermal stabilizers for stabilizing poly(vinyl chloride) / Q. Ye., X. Ma., B. Li [et al.] // Polymers, – 2019, 11 (3), – 531.
15. Egbuchunam T.O., Balköse D., Okieimen F.E. Effect of zinc soaps of rubber seed oil and/or epoxidized rubber seed oil on the thermal stability of PVC plastigels // Polymer Degradation and Stability, – 2007, 92, – p. 1572–1582.
16. Shnawa H.A., Khalaf M.N., Jahani Y. Efficient thermal stabilization of polyvinyl chloride with tannin–Ca complex as bio-based thermal stabilizer / H.A. Shnawa., M.N. Khalaf., Y. Jahani [et al.] // Materials Sciences and Applications, – 2015, 6 (5), – p. 360–372.
17. Shnawa H.A., Jahani Y., Khalaf M.N. Rheological properties of PVC stabilized with tannin-based epoxy resin as non-metallic thermal stabilizer // Polymer Bulletin, – 2017, 74, – p. 1077–1090.
18. Putrawan I.D.G.A., Indarto A., Octavia Y. Thermal stabilization of polyvinyl chloride by calcium and zinc carboxylates derived from byproduct of palm oil refining // Heliyon, – 2022, 8. –e10079.

19. Balköse D., Egbuchunam F., Okieimen E. Thermal behaviour of metal soaps from biodegradable rubber seed oil // Journal of Thermal Analysis and Calorimetry, – 2010, 101, – p. 795–799.
20. Hasanov R.M., Mammadova R.E., Amirov S.A. Effect of sunflower oil-based metal soaps on the thermal stability of polyvinyl chloride / R.M. Hasanov., R.E. Mammadova., S.A. Amirov [et al.] // Eurasian Journal of Chemistry, – 2025, 30 (1), – p. 89–101.

BİOMƏNŞƏLİ PVX TERMOSTABİLİZATORLARININ QARŞILIQLI SİNERGETİKASININ KOLORİMETRİYA İLƏ ÖYRƏNİLMƏSİ

R.M. Həsənov, R.E. Məmmədova

Polivinil xlorid əsaslı kompozit materialların termiki stabilliyinin artırılması üçün termiki stabilizator kimi sintez edilmiş kalsium və alüminium karboksilatlarının birgə istifadəsi zamanı sinergetik effektin baş verib-verməməsinin müşahidə edilməsi üçün kolorimetriyadan istifadə edilmişdir. Müqayisəli qiymətləndirmə üçün ticari NV markalı Ca/Zn stearatları əsaslı termiki stabilizator istifadə edilmiş və yekun nəticədə biomənşəli termiki stabilizatorların hər ikisinin polimerin uzun müddətli termiki stabilliyini yaxşılaşdırdığı, lakin ilkin rəng xüsusiyyətlərinə effektiv təsir göstərmədiyi müəyyənləşdirilmişdir. Termostabilizatorların PVX ilə kimyəvi uyğunluğunun yoxlanılması üçün qarışıqların ərintilərinin qarışıqlardan axması yoxlanılmış və nəticələr alüminium karboksilatının PVX ilə uyğunluğunun yüksək olduğunu, ticari termostabilizatorun isə laylanmaya səbəb olduğunu göstərmişdir.

Açar sözlər: *PVX, termostabilizator, ilkin ağlıq, yaşıl əlavə, kolorimetriya*

ИЗУЧЕНИЕ ВЗАИМНОЙ СИНЕРГЕТИКИ БИОСЫРЬЕВЫХ ТЕРМОСТАБИЛИЗАТОРОВ ПВХ МЕТОДОМ КОЛОРИМЕТРИИ

Р.М. Гасанов, Р.Э. Мамедова

Поливинилхлоридные композиционные материалы были исследованы методом колориметрии с целью выявления наличия или отсутствия синергетического эффекта при совместном использовании синтезированных кальциевых и алюминиевых карбоксилатов в качестве термостабилизаторов для повышения термической стабильности ПВХ. Для сравнительной оценки в качестве эталона был использован коммерческий термостабилизатор на основе стеаратов Ca/Zn марки NV. В результате установлено, что оба биосырьевых термостабилизатора способствуют улучшению долговременной термической стабильности полимера, однако не оказывают эффективного влияния на его начальные цветовые характеристики. Для проверки химической совместимости термостабилизаторов с ПВХ была проведена оценка текучести расплавов смесей. Полученные результаты показали высокую степень совместимости алюминиевого карбоксилата с ПВХ, тогда как использование коммерческого термостабилизатора приводило к расслоению системы.

Ключевые слова: *ПВХ, термостабилизатор, начальная белизна, зелёная добавка, колориметрия*