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Effect of Sunflower Oil-Based Metal Soaps on the Thermal Stability of Polyvinyl Chloride

Calcium and aluminum soaps were synthesized by metathesis method based on sunflower oil, a bio-based raw material, and were applied separately and together to polyvinyl chloride (PVC) as environmentally friendly thermal stabilizers. A number of properties of metal soaps were studied and applied to PVC, and the characterization of the mixtures was carried out using Fourier Transform Infrared Spectroscopy (FTIR). Thermogravimetric and differential thermal analysis (TG-DTA) methods were selected to evaluate the thermal stability of the polymer. A commercial NV-710123-branded thermal stabilizer based on calcium-zinc stearate was selected for the comparative evaluation of the effectiveness of metal soaps. According to the TGA results, the Ca and Al soaps were found to be more effective than the commercial thermal stabilizer. While the pure PVC sample lost 8.93 % of its mass at 269.8 °C, the samples added with Ca, Al soaps, commercial thermal stabilizer and a mixture of Ca and Al soaps at a ratio of 4:1 lost 2.7 % of their mass at 263.5 °C, 3.56 % at 265.7 °C, 4.56 % at 263 °C and 4.12 % at 261.1 °C, respectively. While pure PVC lost more than 44 % of its mass at 300 °C, the mass of the polymer sample with the Al soap added, which was the most effective component at this temperature, decreased by only 16.83 %. This is due to the fact that the Al soap component has a barrier effect and prevents the autocatalytic effect of HCl formed during the degradation of PVC. This allows these components to be used as thermal stabilizers.

Keywords: polyvinyl chloride, thermal stabilizers, sunflower oil, metal soaps, calcium soaps, aluminum soaps, metal carboxylates, thermogravimetry

Introduction

Polyvinyl chloride (PVC) is a general-purpose polymer widely used in the packaging industry, construction materials, cable insulation, and many other industries [1]. According to Our World in Data, the production of PVC was 26.20 million tons in 2000, rising to 51.39 million tons in 2019. This growth trend is forecast to continue at a rate of 3–4 % per year until 2030 [2]. The annual growth of the PVC industry and the growing environmental crisis are increasingly in conflict. The global problem of the PVC industry is its low thermal stability and the release of HCl when it decomposes under temperature. This problem also hinders the recycling of polymer waste by various methods and its use as an energy source [3–6].

Thermal stabilizers are used in the manufacture of PVC-based plastics to prevent thermal degradation. There are many brands of commercial thermal stabilizers with different compositions in the world. The most commonly used thermal stabilizer components in this field are organotin compounds, lead salts, Ca-Ba/Zn stearates, and a number of organic secondary compounds [7, 8]. Each of these compounds has its advantages and disadvantages. For instance, although organic and inorganic lead salts are effective as thermal stabilizers, the addition of heavy metal-containing additives to polymers, as lead-based additives added to gasoline, is limited or completely prohibited [9]. In addition, the PVC processing industry can only produce opaque plastics using lead-based heat stabilizers. The increasing amount of recycled plastics and the need to use them over time makes it essential to use polymer additives accordingly. For example, mixing a lead-containing plastic with a tin-mercaptide-containing plastic can lead to the formation of dark-colored lead sulfides [10]. Mixtures of calcium and barium stearates with zinc stearates are commonly used as alternatives to lead-based compounds. These mixtures exhibit comparable effectiveness as thermal stabilizers to lead-based compounds while being environmentally non-hazardous. Although Ba, Ca and Zn stearates are well studied and environmentally friendly thermal stabilizers, they also have a number of disadvantages. Soaps of these three met-

als are more effective in complex form, but Zn soaps form ZnCl₂ during the thermal degradation of PVC, which catalyzes the decomposition [11–15]. Several studies have been carried out to address this problem. Various secondary compounds have been investigated to prevent the formation of zinc chlorides and to mitigate the catalytic effects of the resulting chlorides [16, 17]. Another proposed solution is to replace zinc with another metal that has a similar thermal stabilizing effect. However, the synthetic nature of these compounds and their high costs in certain regions are additional disadvantages. The search for polymer additives based on renewable raw materials that are environmentally friendly is one of the current topics. Many components based on bio-based raw materials have been synthesized and investigated as thermal stabilizers for PVC, with many positive results. Metal complexes of plant-derived tannins and lignin have been prepared and investigated as PVC thermal stabilizers. Thermogravimetrically, these components have been more effective than commercial thermal stabilizers, and the aromatic and phenolic rings present in their molecular structure also give them antioxidant and photo stabilizer properties [18–20].

Vegetable oils have attracted the most attention as bio-based raw materials. Many studies have been carried out using vegetable oils and their processing industry wastes to synthesize components that can be used as primary and secondary thermal stabilizers. Epoxy vegetable oil obtained from epoxidation of soybean and sunflower oil has been applied as an auxiliary thermal stabilizer component to zinc soaps [21, 22]. In addition, Ca and Zn soaps based on free fatty acids, which are waste products of palm oil refining, have been synthesized and their effects on thermal stability have been evaluated by applying them separately and together to PVC [23]. The results obtained from all these studies are encouraging and, taking them into account, this paper evaluates the effectiveness of Ca and Al soaps synthesized on the basis of sunflower oil, a vegetable oil, as thermal stabilizer components for PVC.

Experimental

Materials

Refined sunflower oil, potassium hydroxide (KOH), ≥ 98 %; ethanol (C₂H₅OH), ≥ 95 %; hydrochloric acid (HCl), 0.1N; calcium chloride (CaCl₂), ≥ 99 %; aluminum sulfate (Al₂(SO₄)₃·18H₂O) ≥ 98 % were used to synthesize metal soaps. To study the thermal stability, PVC synthesized in suspension of the Russian brand RUSVINYL PVC-S was selected, and for the comparative evaluation of the effectiveness of metal soaps, a NV-1710123-branded Ca/Zn-based thermal stabilizer of Chinese production, was used.

Synthesis of Metal Soaps

The synthesis of metal soaps consisted of two stages. In the first stage, water-soluble potassium soap was synthesized from sunflower oil. In the second stage, Ca and Al carboxylates were synthesized by transsaponification and metathesis of water-soluble soap. To synthesize the initial water-soluble soap, a 20 % aqueous alkali solution, 10-20 % above the stoichiometric amount was added to vegetable oil in a reactor system equipped with a reflux condenser and heated. This stage of the process was carried out with intensive heating up to 85–90 °C and mixing. The process gradually became cloudy and eventually took on a heterogeneous form. After 40 minutes, to complete the reaction, the mixture was cooled and ethyl alcohol was added to it. As the process continued with heating and mixing, the heterogeneous mixture gradually became homogeneous and took on an orange transparent appearance. After that, the reflux condenser was turned off to ensure the release of vapors. The solution thickened due to the separation of alcohol and water vapors from the mixture and eventually became a solid mass. The soap was first diluted with water to obtain Ca and Al soaps. After neutralizing the excess alkali with a standard hydrochloric acid solution, CaCl₂ or Al₂(SO₄)·18H₂O solution was added. Since the Ca and Al soaps obtained by trans-saponification were insoluble in water, the solution changed color and became opaque (white). The obtained soaps were dried and Ca soaps were ground and then prepared for application to the polymer.

Study of the Properties of Sunflower Oil and Metal Soaps

A number of properties of sunflower oil were investigated. These were the amount of free fatty acids present in the oil according to ISO 660-220, the iodine value according to ISO 3961-2018, the saponification value according to ISO 3657-2020, and the moisture and volatile content according to ISO 662-2016. The total alkali and acid content of the soluble potassium soap was determined according to ISO 685-2020. The moisture content of Ca and Al soaps and the ash content, including the commercial thermal stabilizer component, were determined.

Application of Thermal Stabilizer Components to PVC and Study of Its Thermal Stability

For the application of Ca (CaSUN) and Al (AlSUN) soaps synthesized from sunflower oil, as well as commercial NV-branded thermal stabilizer to the polymer, 5 phr were used and mechanically mixed with the polymer. The mixtures were melted at 180 °C and 150 bar pressure in an ECOPRESS 102 press device made in Turkey and turned into a homogeneous sample. To compare the compatibility of the thermal stabilizer components with the polymer and the degree of mixing, the samples were observed using an Olympus BX53M optical microscope, manufactured in Germany, with an aperture of 0.8. A NETZSCH STA449F3 Jupiter thermogravimeter, manufactured in Germany, was used to investigate the thermal stability of the samples. Thermogravimetric analysis was carried out in an N_2 gas atmosphere by heating to 900 °C at a heating rate of 30 °C/min. The Fourier Transform Infrared Spectroscopy (FTIR) method was selected to characterize the polymer samples. PerkinElmer Spectrum 100 made in Germany was used for FTIR.

Results and Discussion

Properties of Sunflower Oil and Thermal Stabilizer Components

The sunflower oil used for metal soaps was a food grade oil with a high content of refined linoleic and oleic esters. In order to verify the accuracy of its properties indicated by the manufacturer, the content of free fatty acids, iodine value, saponification value and moisture content were tested. From the results obtained it can be concluded that practically all the fatty acids in the vegetable oil are present in the form of glyceride esters (Table 1).

Table 1

Properties of sunflower oil

Saturated fatty acids, %	Oleic acid, %	Linoleic acid, %	Linolenic acid, %	Free fatty acids, %	Iodine value, g/100g	Saponifica- tion value, mg/g	Moisture, %
10.7	20.7	67.6	≤ 1	0.062	136	191	0.05 %

By checking the total alkali and fat content of the potassium soap synthesized from sunflower oil, it was determined that the saponification of the oil by the above-mentioned method was over 90 %. CaSUN obtained by trans-saponification of potassium soap was a white hygroscopic compound insoluble in water. After drying and grinding, it formed a white-yellowish powder. When stored in the open air, the color darkened to an orange hue due to the oxidation of unsaturated fatty acids, and the powdery mass densified. When kept in an oven at 103 °C, it lost 5.84 % of its mass, which was related to the residual moisture. On the other hand, AISUN was obtained during synthesis as a white, opaque, hydrophobic, and sticky mass. The drying process took longer, and after drying, it took on an orange-transparent, gel-like, viscous fluid form. When stored in the open air, no darkening of its color was observed, and after becoming completely transparent, the residual moisture in the oven at 103 °C was no more than 0.2 %. The residual mass (ash) of the components was determined by subjecting them to combustion in a muffle furnace at a temperature of 1000 °C. The ash percentages for CaSUN and AlSUN were determined to be 8.98 % and 4.98 %, respectively. These results were close to the theoretical values. The ash content of the NV-branded commercial thermal stabilizer component was found to be significantly higher than the theoretical ash content of Ca/Zn stearates. This discrepancy can be attributed to the incorporation of an aluminosilicate additive within the thermal stabilizer complex.

Characteristics of PVC Samples

FTIR was used to characterize PVC samples [24–26]. By comparing the spectra of pure PVC with the spectra of samples with added thermal stabilizer components, significant changes were identified and their causes were investigated. In the FTIR spectrum of PVC (Figure 1), characteristic peaks are observed in the range of 600–800 cm⁻¹ due to the stretching and bending of the C–Cl bond in the base, and peaks in the range of 2850–2960 cm⁻¹ due to the symmetrical and asymmetrical stretching of the bonds present in the polymer chain. All PVC samples have peaks in the corresponding ranges.

When comparing the FTIR spectrum of the PVC sample without a thermal stabilizer component to the FTIR spectrum of the sample with 5 phr commercial thermal stabilizer (Figure 2), changes were observed in the range of 1560–1580 cm⁻¹, corresponding to the asymmetric stretching of the COO⁻ group of metal car-

boxylates, and in the range of 1400–1420 cm⁻¹, related to its symmetric stretching. In the range of 2850–2920 cm⁻¹, the stretching of the carbon chain of fatty acids overlapped with the PVC-specific peaks in this region, potentially causing changes. The peak at 1463 cm⁻¹ originated from the symmetric stretching of the carboxyl groups. The characteristic change for Ca/Zn stearates occurred in the range of 1001–1033 cm⁻¹.

The main changes in the FTIR spectra of polymer samples prepared by applying 5 phr metal soaps synthesized from sunflower oil to PVC were as follows: For PVC/CaSUN (Figure 3), there are peaks at 1574 cm⁻¹, corresponding to the asymmetric stretching of the carboxylate group, and at 1469 cm⁻¹, related to its symmetric stretching. The characteristic peak of PVC at 2920 cm⁻¹ was shifted towards 2905 cm⁻¹. In addition, a peak formed at 1368 cm⁻¹ indicates the presence of metal soaps and the aliphatic chain of fatty acids. The addition of carboxylates overlapped with the peak at 1420 cm⁻¹ resulting from the vibrations of methylene groups. The peak formed at 1716 cm⁻¹ may result from -C=C- or ester-like -C=O bonds, which could be related to the unsaturation of the added plant-based components and they contained the small amounts of unreacted vegetable oil.



Figure 2. FTIR spectrum of PVC with commercial thermal stabilizer (NV-Ca/Zn) added

The FTIR spectrum of AlSUN added PVC (Figure 4) shows similarities with PVC/CaSUN. In this spectrum, there is a peak at 1452 cm⁻¹ corresponding to the symmetric stretching of carboxylates. Changes occurring in the 3000–3100 cm⁻¹ range indicate the formation of unsaturation in the metal soap-added sample. Changes observed in the 1640–1680 cm⁻¹ interval may originate from esters or free fatty acids, suggest-

ing that unreacted plant oil or free fatty acids may be present in the composition of AlSUN. Overall, the addition of metal soaps to the polymer resulted in the appearance of new peaks associated with carboxylates in the spectra, along with various spectral changes influenced by multiple factors.



Figure 4. FTIR spectrum of PVC with added AlSUN

Thermal Stability of PVC

Thermal analysis methods were used to evaluate the thermal properties of the polyvinyl chloride samples. According to thermogravimetric analysis results, the degradation of the polymer samples was a twostage process. In the first stage, the polymer samples lost more than 50 % of their mass. This mass loss is related to the intense dehydrochlorination of the polymer. The polymer sample exhibited a substantial mass loss in the absence of a thermal stabilizer, commencing at 250 °C and persisting until 340 °C. Within this temperature range, a mass loss of 60 % was observed. The TG-DT-DDTA curves of the unmodified PVC sample are shown in Figure 5. PVC lost 5 % of its mass at 260.8 °C, and at 269.8 °C, it reached 8.93 %. Due to the enhanced degradation and the autocatalysis of the resulting HCl, the mass decreased by 38.23 % at 294.8 °C, 44.1 % at 300 °C, and 54.1 % at 320 °C. According to the DDTA results of the polymer samples, the endothermic reactions, i.e., the degradation, intensified starting around 200 °C, and from 245.4 °C to 286.4 °C. The most significant mass loss occurred in this region, as can be seen from the differential TG curves. Analysis of the DTA curves shows that the energy absorption during the first degradation stage was lower than that of the second stage. This observation can be attributed to the fact that the dehydrochlorination of the polymer occurred more readily than the degradation of the polymer chain.

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Figure 5. TG-DT-DDTA curves of a PVC sample without additives

During the degradation of the polymer sample with the added commercial thermal stabilizer, the mass loss occurred at a higher temperature and more slowly compared to the unmodified polymer. The PVC/NV sample lost 4.56 % of its mass at 263 °C, 16.14 % at 288 °C, 28.33 % at 300 °C, 46.44 % at 320 °C, and 58.21 % at 340 °C. The thermal properties of the PVC/NV sample are presented in Figure 6, and as can be seen from the curves, the polymer degradation occurred over a wider temperature range compared to the unmodified polymer according to the DDTA results. The observation that the lowest points of the DDTA curves are higher than those of pure PVC suggests that the thermal stabilizer effectively slowed down the degradation of the polymer in the initial stage. The structure of the DTA curves is similar to that of pure PVC, but the parts of the curves corresponding to energy absorption for PVC/NV correspond to higher temperature ranges. As can be seen from the curves, although the endothermic reactions started at 220 °C, their intensification started at 250 °C and continued up to 301.5 °C. Overall, the intense degradation reactions continued up 347.3 °C. This was significantly higher than in the sample without thermal stabilizer.

The effect of CaSUN and AlSUN components synthesized from sunflower oil on the thermal stability of PVC was positive. The polymer sample with added CaSUN lost 2.7 % of its mass up to 263.5 °C (Figure 7). As heating continued, it lost 16.73 % at 288.5 °C, 27.38 % at 300 °C, 46.5 % at 320 °C, and 56.29 % at 340 °C. At these temperatures, a large proportion of the Cl atoms in the polymer mass had left the polymer chain. The effect of CaSUN on the thermal stability of PVC was similar to that of the commercial thermal stabilizer. However, as shown by the DDTA results, the intensification of endothermic reactions occurred at higher temperatures and at a faster rate compared to the commercial thermal stabilizer. The degradation reactions of the polymer sample with the NV thermal stabilizer component occurred over a wider temperature range and gradually increased in rate. This was due to the Zn soaps in the Ca/Zn mixture producing ZnCl₂, and the increase in the amount of this salt accelerated the degradation. In the samples with added CaSUN, it was assumed that the sudden increase in temperature absorption was related to the abrupt decrease in the concentration of metal soaps during the reaction. When examining the DDTA curves, the value of the lowest point of the endothermic peak in the initial degradation stage of the PVC/CaSUN sample is lower than that of the PVC/NV sample, and this is observed at a relatively lower temperature.



Figure 6. TG-DT-DDTA curves of PVC/NV-Ca/Zn sample



Figure 7. TG-DT-DDTA curves of PVC/CaSUN sample

The effect of AlSUN on the thermal stability of PVC, contrary to expectations, was superior to that of the commercial thermal stabilizer and CaSUN. Specifically, it lost 3.56 % of its mass at 265.7 °C, 11.92 % at 290.7 °C, 16.83 % at 300 °C, 34.89 % at 320 °C and 54.22 % at 340 °C, respectively (Figure 8). Compared to other samples, the mass losses were lower at these corresponding temperatures. When comparing the DDTA curves, the intensity of the endothermic reactions continued up to 316.9 °C, which was the highest value among the samples. In addition, the value of the deepest endothermic peak in the DDTA curves is the

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highest among the other samples, indicating that the initial degradation stage was relatively slow and occurred over a wide temperature range. Contrary to expectations, the formation of metal chlorides that would catalyze the degradation, as seen in Zn soaps, did not occur in the AlSUN component (or occurred later). In contrast, the mass loss of the polymer started at a higher temperature. This suggests that the hydrophobic gellike AlSUN (aluminum soap) component synthesized from sunflower oil positively influenced the thermal stability of the polymer. Its gel form allowed it to form a layer on the surface of polymer segments, protecting them from the effects of Cl and HCl formed during degradation. In short, it played a barrier role against autocatalysis of degradation. This can also be observed under an optical microscope with 5000 K light and a 0.8 aperture diaphragm (Figure 9). The images clearly show that AlSUN had a good compatibility with the polymer and formed a more homogeneous mixture, while the other components were distributed as local inhomogeneous aggregates. The mechanism of the effect of Ca and Al soaps on the stability of PVC is shown in Figure 10.



Figure 8. TG-DT-DDTA curves of PVC/AlSUN sample

As with commercial thermal stabilizer, the use of several thermal stabilizer components together in a mixture provides a synergistic effect. This phenomenon has also been observed in many studies [27–30].

Taking all this into account, to determine how the combination of CaSUN and AlSUN synthesized from sunflower oil would affect the polymer, their respective 4:1 mass ratio mixture was applied to PVC. Although the content of the thermal stabilizer mixture was more compatible with CaSUN, it was more effective in improving the thermal stability of the polymer compared to the individual components. The mass loss of the PVC/Ca-AlSUN(4:1) sample was 4.12 % at 261.1 °C, 12.8 % at 286.1 °C, 22.7 % at 300 °C, 40.16 % at 320 °C, and 55.53 % at 340 °C (Figure 11). When comparing these results to other samples, it can be observed that the combination of these two components was more effective than CaSUN and the commercial NV thermal stabilizer. The mechanism of the mixture effect, as shown in Figure 10, was related to the formation of a barrier on the polymer surface by AlSUN and the neutralization of HCl generated during degradation by CaSUN. It is also evident that the intensities of heat release and absorption in the DDTA curves vary significantly over a wide range, indicating the complexity of the process. The values of the endothermic peaks are also higher compared to the other samples, suggesting a lower intensity of degradation. The DTA curves also show that there was no sharp energy absorption during the initial degradation stage, which further supports the previous observations. In summary, the temperatures corresponding to 5 %, 10 %, 20 %, and 50 % mass loss for all the samples analyzed are presented in Table 2.

It can be determined from the optical microscope images of polymer samples with CaSUN and AlSUN components mixed in ratios of 3:1, 4:1, and 5:1, that as the proportion of AlSUN in the mixture increased, a more homogeneous mixture with the polymer was obtained (Figure 12). This suggests that the compatibility of Al soap with PVC was better than that of the Ca soap.







Aluminium soaps barrier for autocatalysis

Figure 10. Mechanisms of influence of CaSUN and AISUN on the thermal stability of PVC

Comparing the DTG with a 20 °C interval and the DTA curves (Figures 13 and 14), it can be seen that degradation was most intense in the pure polymer sample. In the DTG curves, the curves for the polymer sample with CaSUN and the polymer sample with the NV commercial thermal stabilizer overlapped on the temperature axis, but degradation occurred more intensively in the sample with CaSUN. When examining the DTG curve of the sample with AlSUN, it is evident that although degradation was intense, it occurred at a higher temperature compared to the other samples. Among the polymer samples, the sample with the Ca-AlSUN mixture showed the lowest intensity of degradation.





Figure 11. TG-DT-DDTA curves of PVC/Ca-AlSUN (4:1) sample



(a) PVC/(CaSUN:AISUN)(3:1) (b) PVC/(CaSUN:AISUN)(4:1) (c) PVC/(CaSUN:AISUN)(5:1)

Figure 12. Optical microscope images of PVC samples containing Ca-AlSUN in different ratios

A similar result was obtained when comparing the DTA curves. Upon consideration of the energy absorption during the intensification of the degradation reactions, it can be seen that the polymer sample without additives decomposed at a lower temperature. In the sample containing CaSUN, the intensification of degradation began earlier than in the sample containing the commercial NV thermal stabilizer. Among all the samples it can also be seen from the comparison of the DTA curves that the sample containing AlSUN was which the degradation intensified the latest. In general, it can be seen that the endothermic reactions occurred more slowly in the polymer sample containing the Ca-AlSUN mixture. These findings suggest that the combined use of the two metal soaps leads to a synergistic effect. However, the results obtained and the analysis methods employed do not provide sufficient information to evaluate the color properties of the polymers.

Table 2

Somm10	Mass loss						
Sample	5 %	10 %	20 %	50 %			
PVC-pure	256.56	270.71	279.25	313.14			
PVC/NV	263.95	274.74	292.07	328.36			
PVC/CaSUN	267.60	276.51	291.41	323.73			
PVC/AISUN	270.01	284.96	301.46	335.19			
PVC/Ca-AlSUN(4:1)	263.63	278.04	295.66	333.57			

Temperatures Corresponding to 5 %, 10 %, 20 %, and 50 % Mass Loss of Samples, °C



Figure 13. DTG curves of polymer samples at 20 °C intervals



Figure 14. Comparison of DTA curves of polymer samples

The research found that Ca and Al soaps synthesized from sunflower oil, a plant-based raw material, improved the thermal stability of PVC as thermal stabilizer components. Compared to NV-branded $CaSt_2$ and $ZnSt_2$ based commercial thermal stabilizer, the metal soaps synthesized from vegetable oil showed several advantages. All this demonstrates the possibility of synthesizing effective polymer additives from renewable resources.

Conclusions

In order to find environmentally friendly, effective, and cost-efficient thermal stabilizer components for PVC, the effect of Ca and Al soaps synthesized from sunflower oil as renewable resource on the thermal sta-

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bility of the polymer was investigated. When polymer samples were heated to 300 °C, the polymer sample without additives lost 44.1 % of its mass, while the polymer sample containing a commercial thermal stabilizer lost 28.33 %, the sample containing Ca soap synthesized from sunflower oil lost 27.38 %, the sample containing Al soap lost 16.83 %, and the sample with a mixture of Ca and Al soaps in a 4:1 weight ratio lost 22.7 %. The Ca soaps provided thermal stability by neutralizing HCl, while the Al soaps formed a layer on the surface of the polymer particles, providing a barrier effect. This reduced the autocatalytic effect of HCl generated during degradation. The using these soaps together produced a synergistic effect. This scientific research demonstrated that vegetable oils can be a potential resource for synthesizing polymer additives.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Roman Manar Hasanov** conceptualization, data curation, investigation, methodology, funding acquisition, resources, visualization, writing original draft and editing; **Rasmiyya Elbrus Mammadova** data curation, formal analysis, supervision, validation; **Sabir Qarash Amirov** data curation, formal analysis, validation, supervision; **Zumrud Davud Aliyeva** conceptualization, data curation, investigation, methodology, formal analysis.

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Conflicts of Interest

The authors declare no conflict of interest.

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