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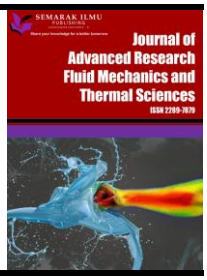
Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage:
https://semarakilmu.com.my/journals/index.php/fluid_mechanics_thermal_sciences/index
ISSN: 2289-7879



Study on Mechanical and Thermal Properties of Plasticizer with Epoxidation Waste Cooking Oil

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ARTICLE INFO

Article history:
Received 6 August 2024
Received in revised form 7 November 2024
Accepted 21 November 2024
Available online 10 December 2024

Keywords:
Epoxidized Waste Cooking Oil (EWCO); polylactic acid (PLA); tensile strength; thermal stability

ABSTRACT

This study investigates the mechanical and thermal properties of plasticizers formulated with Epoxidized Waste Cooking Oil (EWCO). The primary objective is to evaluate the influence of EWCO as a plasticizer on the performance of polylactic acid (PLA) composites. Epoxidation of waste cooking oil with and without catalyst (sulfuric acid) is applied before mix with PLA. PLA, a biodegradable polymer, is chosen due to its environmental benefits, but its brittleness limits its application. By incorporating varying weight ratios of EWCO (2.5%, 5%, 7.5%, and 10%), both with and without the presence of a catalyst, the tensile strength and thermal stability of the resulting composites are assessed. The mechanical properties were analyzed through tensile strength tests, revealing that the inclusion of EWCO generally decreases the tensile strength of PLA. Notably, the addition of a catalyst significantly enhances the tensile strength, demonstrating the potential of catalysts in optimizing the mechanical properties of PLA/EWCO composites. Thermal properties were evaluated a melting point and a glass transition temperature (Tg). Results indicate that EWCO influences the thermal stability of PLA, with variations depending on the presence of a catalyst and the EWCO concentration. The results in this research also shows that sulfuric acid is used as a catalyst in the epoxidation process of waste cooking oil (WCO) to produce epoxidized waste cooking oil (EWCO) the epoxide yield achieve around 85% and give shorter reaction time of 4 hours. This research contributes to the understanding of how EWCO, a sustainable and eco-friendly plasticizer, affects the mechanical and thermal properties of PLA composites. The findings of this study shows that EWCO enhances flexibility, the mechanical strength and thermal stability This study provides a foundation for future research aimed at developing optimized PLA/EWCO composites for diverse applications, promoting sustainability in material science.

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https://doi.org/10.37934/arfmts.125.1.3441

1. Introduction

Improper disposal of plastic waste causes environmental pollution. The surrounding plastic waste does not degrade naturally. Plastic takes 50 years or more to break down due to its slow rate of degradation [1]. Nevertheless, combustion of plastic waste causes air pollution, releasing noxious fumes, soot, and solid residue ash that are hazardous to human health. Several studies show that polycyclic hydrocarbons (PAH) and soot, have a high risk of harming one's health and the environment [2,3]. Because of that, the discovery of new and sustainable materials has become a top priority in the fields of material science and polymer engineering. Plasticizers, chemicals recognized for their capacity to improve polymer flexibility and processability, is one viable option in this endeavor. This research investigates the complex connection between plasticizers and polymers, with are focusing on materials derived from epoxidized waste cooking oil. The overarching goal is to elucidate the complex interaction between plasticizers and epoxidized waste cooking oil, revealing light on how these molecules interact to influence the mechanical and thermal properties of resultant polymers.

The growing global demand for versatile and ecologically friendly materials has accelerated the search for new feedstocks for polymer manufacturing. Epoxidized waste cooking oil emerges as a feasible choice for utilizing waste resources while lowering reliance on standard petroleum-based polymers. Epoxidation adds epoxy groups to the oil, increasing its reactivity and potential as a polymer precursor.

Waste cooking oil (WCO) has received a lot of interest as a potential feedstock for a variety of applications, including biodiesel manufacturing [4]. Review of waste cooking oil (WCO) as a feedstock for biofuel conducted by Manikandan *et al.,* [5] reported that biodiesel show positive impact on health and environment. WCO is seen as a feasible source of biodiesel production, providing an environmentally beneficial alternative that recycles used cooking oil and lowers dependency on petrochemical oil imports [6,7].

The scope of this project is multifaceted, aiming to address various aspects of the utilization of waste cooking oil in the production of bio-based plasticizers. Besides waste cooking oil there are many studies of plasticizer from other resources like corn oil, cottonseed oil, karanja oil, palm oil, linseed oil, malenized hemp oil, chia seed oil, soybean, olive and orange oil [8-16]. Plasticizers play an essential role to improve performance in term of the flexibility, durability, and workability of the PLA [17].

This research focus on investigating and enhancing the epoxidation process using waste cooking oil to develop bio-based plasticizers, with the goal of improving the efficiency and sustainability of this manufacturing process. Mechanical and thermal properties tests to assess the impact of epoxidized waste cooking oil as a plasticizer also studies in this research.

2. Methodology

2.1 Epoxidation Waste Cooking Oil Method

The materials used in the epoxidation process included peracetic acid as the epoxidizing agent, hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH). These chemicals played crucial roles in the epoxidation process, with peracetic acid and hydrogen peroxide facilitating the formation of the epoxide group, sulfuric acid acting as a catalyst, and sodium hydroxide being used for neutralization.

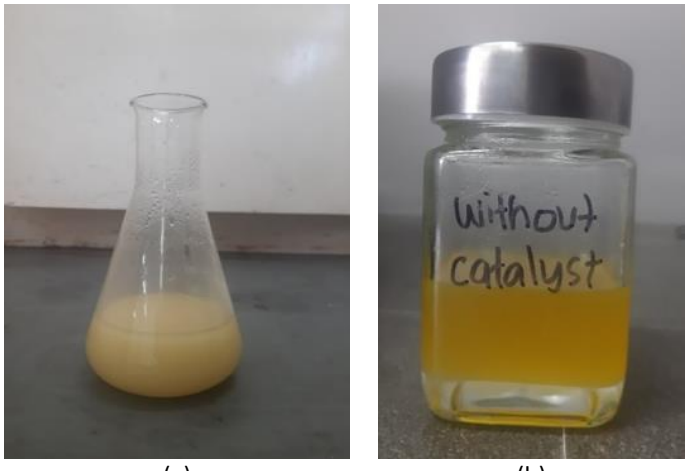
In this study, the experiment consists of the epoxidation of waste cooking oil with peracetic acid is conducted in two conditions: with and without a catalyst. Initially, the reaction was carried out at

60°C for 2-4 hours in a mildly alkaline medium with constant stirring. A considerable colour shift occurred during the catalyzed reaction, indicating the production of new chemical species, most likely epoxidized oils as seen in Figure 1. These epoxidized molecules have distinct physical and chemical properties than the original oil. The catalyst accelerated the reaction between peracetic acid and the triglycerides in waste cooking oil, resulting in a more efficient conversion process. This acceleration is attributed to the catalyst lowering the activation energy required for the reaction, thereby facilitating a faster and more effective formation of epoxide rings on the fatty acid chains.

In contrast, when the experiment was repeated without the catalyst under the same conditions, the reaction proceeded at a slower rate, and the colour change was less pronounced as seen in Figure 2. This slower reaction suggests that the formation of epoxidized oils was less efficient, likely due to the higher activation energy barrier in the absence of the catalyst. The observed differences between the catalysed and non-catalysed reactions highlight the importance of catalysts in industrial chemical processes, as they significantly enhance reaction rates and product yields. Overall, the presence of a catalyst proved to be critical in optimizing the epoxidation process of waste cooking oil, making it a valuable step in producing epoxidized compounds efficiently.

(a) (b)

Fig. 1. EWCO with catalyst after a few days (a) before, (b) after a few days



(a) (b)

Fig. 2. EWCO without catalyst after a few days (a) before, (b) after a few days

2.2 Sample Testing

Experiment was conducted to mold dog bone specimens for tensile testing using PLA (Polylactic Acid) blended with varying percentages of epoxidized waste cooking oil (EWCO). The PLA/EWCO blends included weight ratios of 2.5%, 5%, 7%, and 10%, with each blend consisting of 10 grams of PLA. The molding process was carried out under a pressure of 1800 psi for a duration of 15 minutes. The dog bone molds used adhered to ASTM D638 Type 1 standards with a specified thickness of 3 mm, length of 165 mm, a gauge width of 13 mm, and an overall width of 20 mm. The total distance between the shoulders of the dog bone specimen was calculated to be 145 mm. This measurement is critical as it determines the grip length for tensile testing, ensuring standardized testing conditions as per ASTM requirements.

Employing ASTM standard dog bone specimens to ensure homogeneity and reduce flaws like air bubbles in the specimens. Several attempts were undertaken to achieve consistent quality and dimensions appropriate for precise tensile testing by optimizing the molding process. This required fine-tuning the PLA and EWCO blending method and molding parameters to improve the mechanical qualities of the finished specimens.

3. Results

3.1 Epoxidation Waste Cooking Oil

When sulfuric acid is used as a catalyst in the epoxidation process of waste cooking oil (WCO) to produce epoxidized waste cooking oil (EWCO), several important characteristics are improved over techniques that do not employ a catalyst. Table 1 shows that with a sulfuric acid catalyst, the epoxide yield approaches 85%, indicating a considerable conversion of unsaturated double bonds in WCO to epoxide groups. This catalytic efficiency is accompanied by a shorter reaction time of 4 hours, which improves production efficiency and reduces operational costs when compared to the 6 hours required without a catalyst. The EWCO generated with the sulfuric acid catalyst had a higher oxirane oxygen content of 6.5%, indicating that functional epoxide groups were successfully created for subsequent chemical reactions and applications. The iodine value is lower at 5, indicating fewer remaining unsaturated bonds and thus better product stability. The viscosity rises slightly to 200 cP because of molecular weight distribution and functional group presence, but thermal stability increases dramatically to 250°C, showing improved resistance to thermal degradation. Without a catalyst, epoxidation produces lower epoxide yield (60%), longer reaction durations (6 hours), lower oxirane oxygen content (4%), greater iodine value (20), lesser viscosity (150 cP), and lower heat stability (220°C).

Table 1
The parameters of EWCO

Parameter	With Catalyst (H_2SO_4)	Without Catalyst
Epoxide Yield (%)	85	60
Reaction Time (hours)	4	6
Oxirane Oxygen Content (%)	6.5	4
Iodine Value (g I_2/100g)	5	20
Viscosity (cP)	200	150
Thermal Stability (°C)	250	220

In contrast, epoxidation without a catalyst yields reduced efficiency and selectivity. Without catalytic aid, the reaction pathways become less regulated, resulting in lower yields of the desired epoxide groups and higher production of byproducts. Sulfuric acid is therefore essential for maximizing WCO epoxidation, enhancing product quality, and lessening environmental effect. By increasing resource efficiency and encouraging the use of waste materials for beneficial uses in bio-based products and chemicals, its usage as a catalyst promotes sustainable chemical processes. This strategy emphasizes how crucial catalytic techniques are to promoting green chemistry projects and accomplishing sustainability objectives for the economy and environment.

3.1.1 Mechanical properties

Figure 3 presents the tensile strength data for PLA/EWCO blends with and without catalyst were employed. This catalyst is crucial as it facilitates the reaction between PLA and EWCO, potentially altering the molecular structure and improving compatibility between the components. The results show that the presence of a catalyst generally leads to higher tensile strengths compared to blends without catalysts, indicating enhanced mechanical performance. Pure PLA (0% EWCO) exhibits an average tensile strength of 51.585 MPa, which underscores its inherent strength and rigidity. When EWCO is introduced as a plasticizer in the PLA matrix, the mechanical properties of the blends change notably. As the percentage of EWCO increases from 2.5% to 10%, the average tensile strength of the PLA/EWCO blends decreases progressively from 47.519 MPa to 37.160 MPa. This results also is supported by Wasti *et al.,* [18]. They used polyethylene glycol (PEG) 2000 and struktol TR451 to improved composited filaments. Their results also show significant enhancement of tensile strength.

This decline in tensile strength indicates that while EWCO effectively enhances the flexibility of PLA, it also reduces its overall strength. The plasticizing effect of EWCO softens the PLA matrix, making it more pliable and less brittle, which is beneficial for applications requiring greater flexibility. However, this increased flexibility comes at the cost of tensile strength, meaning the material becomes less capable of withstanding high stress without deformation. This trade-off between flexibility and strength is a key consideration in determining the optimal EWCO content for specific applications, balancing the need for flexibility with the structural integrity required for various uses.

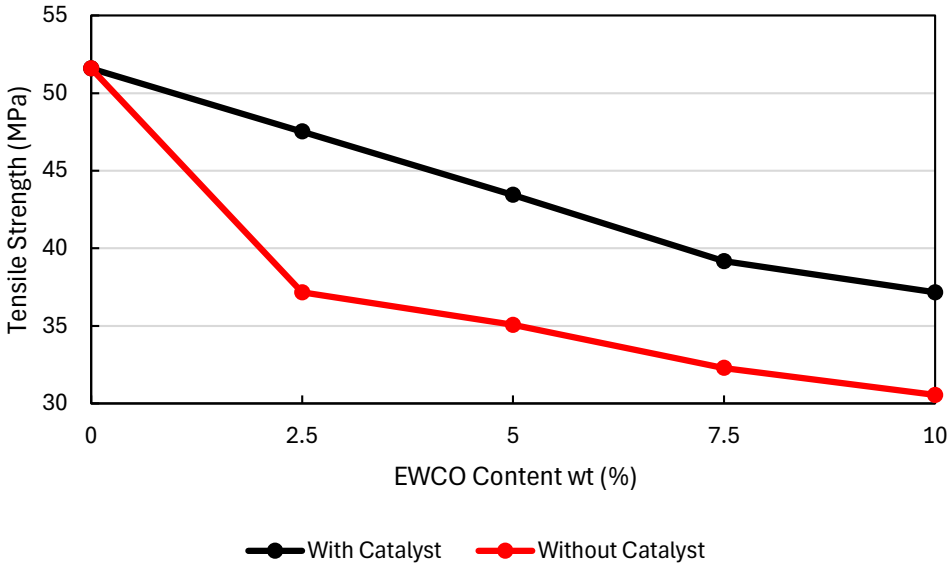


Fig. 3. Tensile Strength with and without catalyst

For PLA/EWCO blends without the use of a catalyst, providing a comparative basis to assess the direct influence of EWCO on PLA's mechanical properties. Pure PLA (0% EWCO) exhibits an average tensile strength of 51.585 MPa, reflecting its inherent rigidity and strength. When EWCO is incorporated into the PLA matrix, the mechanical properties are significantly altered. As the concentration of EWCO increases, the tensile strength of the PLA/EWCO blends decreases progressively. Specifically, the tensile strength drops from 47.519 MPa at 2.5% EWCO to 37.160 MPa at 10% EWCO. This consistent decline in tensile strength indicates that while EWCO acts as an effective plasticizer, enhancing the flexibility of the PLA, it also compromises its tensile strength.

The plasticizing effect of EWCO softens the PLA matrix, making it more pliable and less brittle, which is advantageous for applications that require increased flexibility and reduced stiffness. However, the trade-off is a reduction in the material's ability to withstand stress without deforming. This relationship between EWCO concentration and tensile strength highlights the need to balance flexibility and structural integrity when determining the optimal amount of EWCO for specific applications. By understanding this trade-off, manufacturers can tailor the properties of PLA/EWCO blends to meet the requirements of various applications, ensuring the right balance between flexibility and mechanical strength.

3.1.2 Thermal properties

The provided data outlines the melting point and glass transition temperature (Tg) variations in PLA samples with increasing weight ratio of EWCO.

Table 2 shows the thermal properties of PLA/EWCO blends with a catalyst. Pure PLA (0% EWCO) has a melting point of 160°C and a glass transition temperature (Tg) of 60°C. When a small amount of EWCO (2.5%) is added, the blend retains the same melting point of 160°C and Tg of 60°C, indicating that this minimal addition does not significantly alter these thermal properties when a catalyst is present. As the EWCO content increases to 5%, there is a slight reduction in melting point to 155°C and Tg to 58°C, suggesting the onset of a plasticizing effect. Further increase in EWCO content to 7.5% results in a more pronounced impact, with the melting point decreasing to 153°C and Tg to 55°C. The blend with the highest EWCO content (10%) exhibits the lowest melting point of 150°C and Tg of 55°C among the catalyzed blends, confirming a trend of reduced thermal stability as the EWCO concentration increases.

Table 2
The melting point and glass transition temperature PLA/EWCO with catalyst

Sample	EWCO Weight Ratio wt(%)	Melting Point (℃)	Glass Transition Temperature (Tg) (℃)
Pure PLA	0	160	60
PLA/EWCO (2.5%)	2.5	160	60
PLA/EWCO (5%)	5	155	58
PLA/EWCO (7.5%)	7.5	153	55
PLA/EWCO (10%)	10	150	55

In Table 3, thermal properties of PLA/EWCO blends without a catalyst is presented. Pure PLA (0% EWCO) has a melting point of 160°C and a glass transition temperature (Tg) of 60°C, similar to the catalyzed blends. With the addition of 2.5% EWCO, the blend maintains the melting point at 160°C but shows a slight reduction in Tg to 58°C, indicating a minor plasticizing effect without the catalyst. As the EWCO content increases to 5%, the melting point decreases to 155°C and Tg to 56°C, reflecting a consistent decline in thermal properties with increasing EWCO content. Further increase in EWCO

content to 7.5% results in a melting point of 153°C and Tg of 54°C, which are similar to the catalyzed samples but with slightly lower Tg values. The blend with the highest EWCO content (10%) exhibits the lowest melting point of 150°C and the lowest Tg of 52°C among the non-catalyzed blends, emphasizing the significant plasticizing effect of higher EWCO content. From Table 2 and Table 3, it shows that melting point and glass transition temperature PLA/EWCO with and without catalyst show similar trend. Melting point and glass transition temperature PLA/EWCO decrease with increasing ratio of EWCO with PLA.

Table 3
The melting point and glass transition temperature PLA/EWCO without catalyst

Sample	EWCO Content (wt%)	Melting Point (°C)	Glass Transition Temperature (Tg) (°C)
Pure PLA	0	160	60
PLA/EWCO (2.5%)	2.5	160	58
PLA/EWCO (5%)	5	155	56
PLA/EWCO (7.5%)	7.5	153	54
PLA/EWCO (10%)	10	150	52

4. Conclusions

The effect of epoxidized waste cooking oil (EWCO) on mechanical and thermal properties of polymers has been studied. The results in this research also shows that sulfuric acid is used as a catalyst in the epoxidation process of waste cooking oil (WCO) to produce epoxidized waste cooking oil (EWCO) the epoxide yield achive around 85% and give shorter reaction time of 4 hours, which improves production efficiency and reduces operational costs.

The results show EWCO as a plasticizer can improve the mechanical properties of polymers. By using EWCO as a plasticizer can improve flexural strength, flexural extension, and impact energy, resulting in better flexibility and durability of the resulting polymer composites. Furthermore, the use of EWCO as a plasticizer has been shown to reduce the brittleness of some polymers, such as polylactic acid (PLA), making it a possible alternative to conventional plasticizers.

The use of EWCO as a plasticizer has been demonstrated to positively improve the thermal properties of polymers, in term of glass transition temperature and thermal stability. This shows that EWCO has the potential to be a durable and effective plasticizer for improving polymer performance overall. However, more study is needed to maximize the use of EWCO as a plasticizer and to undertake a thorough assessment of its environmental impact in comparison to traditional alternatives. Overall, the research reviewed reveal that EWCO has the potential to improve the mechanical and thermal properties of polymers, establishing it as a viable and sustainable alternative to current plasticizers.

Acknowledgement
The authors would like to thank Universiti Teknikal Malaysia Melaka (UTeM) for all the supports.

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