Characterization of Modified PALF Composites for Eco-Friendly Food Packaging

[1] Rubiyah Baini; [2] Sariah Abang & [3] Sii Siew Ping
[1,2,3] Department of Chemical Engineering and Energy Sustainability, Universiti Malaysia Sarawak, Malaysia

Corresponding Author: Rubiyah Baini

Abstract: This study investigated the suitability of pineapple leaf fibre (PALF) as a sustainable raw material for paper-based food packaging by evaluating the effects of pulping duration, NAOH treatment, and natural additives on structural, chemical, thermal, and morphological properties. It was found that complete pulping occurred at 90 minutes, producing a smooth, uniform paper surface. Additives including eggshell powder, sago starch, and glycerol were assessed for their ability to enhance paper appearance and performance. FTIR analysis confirmed compounds associated to cellulose, hemicelluloses and lignins and incorporation of additives into the fibre matrix. SEM images showed improved fibre bonding with starch and enhanced rigidity with eggshell powder, while glycerol acted as a plasticizer increasing flexibility. Thermal analysis demonstrated that eggshell-treated samples provided the highest thermal stability and residue content, whereas glycerol lowered decomposition temperature. Overall, the findings indicate that NAOH-treated PALF reinforced with eggshell powder offers the most balanced combination of strength, thermal stability, and barrier properties, making it a promising biodegradable alternative for food packaging applications.

1.0 Introduction

Global plastic production has increased sharply, rising from 368 to 400 million tons in 2019 to 2022, and is projected to reach 800 million tons in 2050, reflecting extensive global use of plastic material (Pilapitiya and Ratnayake, 2024). Discarded plastics have generated massive quantities of waste, estimated at 6.30 billion tons from 1950 to 2015, and approximately about 242 million tons in 2016 alone(Liang et al., 2021).Annual plastic waste generation is predicted about 1.7-1.9 billion tons per year (Fayshal et al., 2023). The concerning reality about the massive plastic waste is it's slow degradation rates range from 100 to 1000 years (Chamas et al., 2020), which reached an alarming stage. Plastic waste exist in both macro and nano sizes that can have detrimental impacts to the environment and human health (Pilapitiya and Ratnayake, 2024).

Packaging has been identified as the most significant contributor, accounting for about 50% of the total global plastic waste (Ncube et al., 2021), primarily due to the short-lived, single-use nature of most packaging materials. The widespread use of plastic packaging contributes to serious environmental threats, including land and marine pollution, greenhouse gas emissions from production and incineration, and harm to both wildlife and human health due to microplastic contamination.

Growing concerns over plastic pollution have intensified the global search for sustainable and biodegradable alternatives materials. Natural fibers derived from agricultural by-products offer a promising solution. Among these, pineapple leaves, which available in abundance, fibrous in nature and commonly discarded as agricultural waste is a significant potential. Global pineapple production shows an increasing trend, exceeding 25 million tons in 2020, with projections of more than 30 million tons by2030, and 50% of the production comes from Asia (Tran et al., 2023). Pineapple leaves represent the largest portion of the plant, and are commonly left to decompose in the field or burned. According to Kenkhetkit and Amornsakchai (2014), in Thailand alone, approximately 20,000 to 25,000 tons of pineapple leaves per acre remain in situ after harvesting. Pineapple leaves contain chemical compositions suitable for papermaking with 20-80% of cellulose, 10-20% hemicellulose, and 3-14% lignin (Saini, 2023). Pineapple leaf Fibre (PALF) also exhibits excellent mechanical properties, which have encouraged its application in reinforced polymer composites, low-density polyethylene blends, and biodegradable plastics.Reported mechanical properties include a tensile strength of 413-1627 MPa and Young's Modulus of 60-82 GPa (Mwaikambo, 2006).

Despite this potential, several challenges remain in optimizing the use of pineapple leaves for food packaging applications. Papers derived from PALF often lack sufficient strength, durability, and water resistance, the properties that are essential for functional food packaging. Furthermore, efficient processing techniques and cost-effective production methods are needed for large-scale implementation. Currently, there is limited research on strategies to enhance the physical and mechanical properties of PALF paper to meet commercial packaging standards.

The development of biodegradable packaging solutions from agricultural waste such as pineapple leaves also supports several United Nations Sustainable Development Goals (SDGs). Specifically, this research aligns with SDG 12: Responsible Consumption and Production, by promoting the use of renewable resources and minimizing waste. It supports SDG 13: Climate Action, by reducing reliance on fossil fuel-based plastics and lowering greenhouse gas emissions. Moreover, it contributes to SDG 15: Life on Land, by utilizing agricultural residues and reducing environmental pollution from both plastic and organic waste.

Ultimately, creating high-quality, biodegradable packaging solutions from agricultural waste represents a significant step toward mitigating plastic pollution and fostering sustainability in the packaging industry. This research not only addresses urgent environmental challenges but also promotes circular-economy practices

through the valorization of agricultural by-products, contributing to a more sustainable future. In this work, several formulations were proposed incorporating sodium hydroxide (NaOH), glycerol, and additives to enhance the properties of the developed paper-based packaging material.

2. Methodology

Pineapple leaves were obtained from a nearby pineapple farm in Kota Samarahan. The fresh leaves were cleaned, oven-dried at 70°C for 24 hours, and cutinto aaproximately 5 cm segments. For each experiment 5g of dried pineapple leaves were mixed with sodium hydroxide (NaOH)solution, and boiled at 100°C. The pulping process was conducted using NaOH at concentrations of 1%, 2%, and 3% w/w with pulping durations of45, 60, or 90 minutes. Following pulping, the fibers were washed thoroughly with tap water, and blended for approximately five minutes to produce a uniform fine slurry. This blending process facilitates the release of cellulose fibers from the leaf matrix, yielding a smooth and homogeneous pulp suitable for sheet formation. Sago starch (SS) and eggshell (EG) powder (1, 3 and 8 g) weresubsequently incorporated into the pulp. The mixture was then poured onto a wire mesh mold and pressedto remove the excess water, forming a paper sheet. The sheets were oven-dried at 50°C for 3 hours. Glycerol (Gly) was applied uniformly onto the surface of the dried sheets to serve as acoating and improved plasticizer, and the papers were left to dry at room temperature for 24 hours. Glycerol concentration of18%, 22.5% and 27% were used.

The produced papers were evaluated for their physical, mechanical, morphological and and biodegradability properties. Morphological analysis was conducted using scanning electron microscopy (SEM). Thickness measurements were performed using a Vernier Calliper followingAPPI T411 and ISO 534 standards. Papergrammage was determined accordingto ISO 536 and TAPPI T410. Water absorbency was assessed following ISO 535 (Cobb test) while grease resistance was evaluated using TAPPI T559 method. Biodegradability was analysed based on ISO 14855 and EN 13432 standards. Antimicrobial activity was assessed using a modified procedure based on ASTM E2149 and ISO 22196.

3. Results and Discussion

3.1 Visual Observation

The appearance of papers produced using different cooking times are shown in Figure 1. For cooking time of 45 minutes (Figure 1a), the sample still contain noticeable fibers, indicating that the pulping process is incomplete. The raw materials have not been fully broken down, resulting in a rough texture due to the partially intact fiber structure. This suggests that the cooking time is insufficient to create a uniform pulp necessary for high-quality paper production. For cooking time of 60 minutes (Figure 7b), the paper exhibited fewer visible fibers compared to that for 45minutes. The longer duration of cooking time used allowing greater breakdown of the fibrous

material, leading to a more consistent surface. However, slight traces of fibers remain, implying that the pulping is close to completion but not yet fully optimized. This stage marks significant improvement in texture and uniformity. For 90 minutes cooking time (Figure 7c), the paper showed a completely smooth surface with no visible fibers, indicating thorough pulping. The extended cooking period has fully disintegrated the fibers, producing a refined and homogeneous texture. This smooth finish signifies that the optimal pulping conditions have been achieved, underscoring the importance of adequate cooking time for producing high-quality paper.For 180 minutes (Figure 7 d), no significant visual change was observed compared to that for 90minutes. The paper maintained the same smooth surface and uniform texture, suggesting that the pulping process had already reached completion by 90 minutes. This suggests that extending the cooking time beyond 90 minutes does not further improve the appearance or quality of the paper.

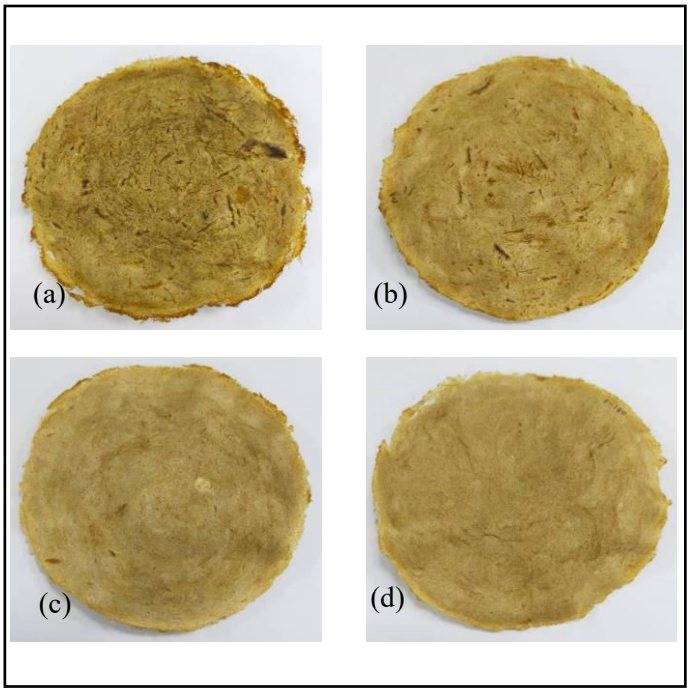

Figure 1. Papers for different cooking time: (a)45 mins; (b)60 mins; (c)90 mins; (d)180 mins

Figure 2 presented the visual characteristics of paper subjected to different treatments: (a) without additives, (b) with eggshells, (c) with sago starch, and (d) bleached with 1% hydrogen peroxide. The sample without any additives (Figure 2a) had a smooth texture, indicating that the fundamental pulping process effectively broke down the fibers. However, it retained a darker color, likely due to the inherent pigmentation of the raw materials, as no bleaching agents were used to alter its appearance.When eggshells powder is incorporated (Figure 2b), the paper appeared lighter in color compared to the untreated sample, but the surface became slightly crinkled. This uneven texture may result from the coarse or uneven dispersion of

eggshell particles, while the brightness can be attributed to the presence of calcium carbonate in the eggshells, which acts as a natural whitening agent.The paper containing sago starch (Figure 2c) demonstrated a smoother surface and an even paler color than both the untreated and eggshell-treated samples. Sago starch functions as a binder, promoting a more uniform and cohesive paper structure, and also contributes to the lightening effect due to its natural whitening capabilities.The sample bleached with 1% hydrogen peroxide, H_2O_2 (Figure 2d) was observed to be the whitest of all, reflecting the strong bleaching capacity of this chemical. H_2O_2 effectively degrades the compounds responsible for coloration in the pulp, resulting in a much brighter and cleaner appearance. Despite this chemical treatment, the texture remains smooth, suggesting that the structural quality of the paper is preserved. This method is particularly suitable for paper types that require high brightness, such as those used for printing or writing. The amount of H_2O_2 need to be adjusted to obtain desired whiteness.

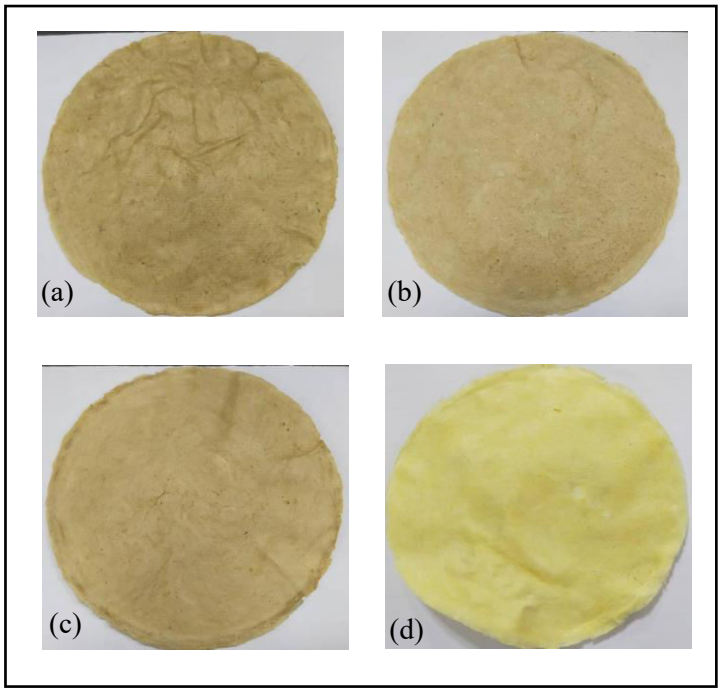

Figure 2. Papers with additives: (a)no additives; (b)ES; (c)SS; (d)H_2O_2

3.2 FTIR Analysis

The FTIR spectrum of the NaOH-treated pineapple leaves are shown in Figures 3 - 7. FTIR spectra of all treated PALF samples exhibited characteristic lignocellulosic bands, confirming absorption bands associated with cellulose, hemicellulose and lignin fractions indicating the presence of O-H, C-H, C=O and C-O functional groups. Based on McMurry (2012), the broad O–H stretching band is within 3200–3600 cm^{-1}, C-H stretching within 2850-3000 cm^{-1}, C=O stretching at 1700 cm^{-1}, C-O absorption in the fingerprint region within 400-1500 cm^{-1}, and absorption bands within these bands have been observed in the FTIR spectra of PALF samples shown in figures below. Similar observations on characteristics of hemicellulose, sellulose and lignin were found by

Chaves et al., (2024), Tanpichai and Witayakran (2017) and Yang et al., (2007).Addition of sago starch intensified the O–H band and the fingerprint region due to its high hydroxyl content and glycosidic linkages, which introduce more C–O–C vibrations. This enhancement suggests improved hydrogen bonding potential between fibers, which is beneficial for paper sheet formation. Incorporation of glycerol further broadened and deepened the O–H absorption, reflecting its polyol nature, and introduced additional CH stretching peaks. These changes indicate increased hydrophilicity and flexibility, as glycerol disrupts intermolecular hydrogen bonding, reducing brittleness. The addition of eggshell powder relates to the addition of calcium carbonate ($CaCO_3$) compound associated with the signals in the 745–500 cm^{-1}region (Vagenas et al., (2003), indicating successful incorporation of mineral particles into the fiber matrix.

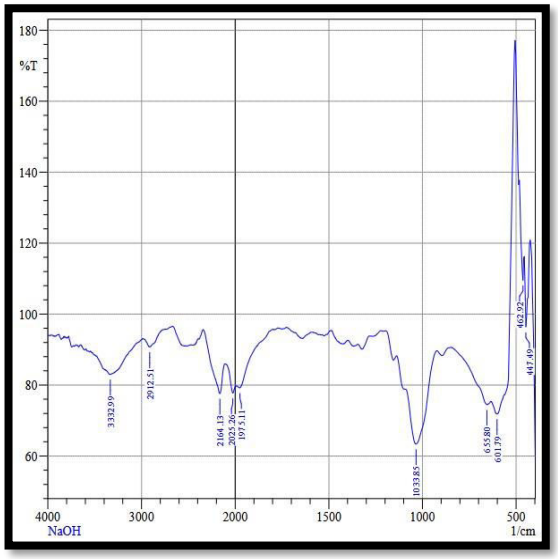

Figure 3: FTIR-NAOH

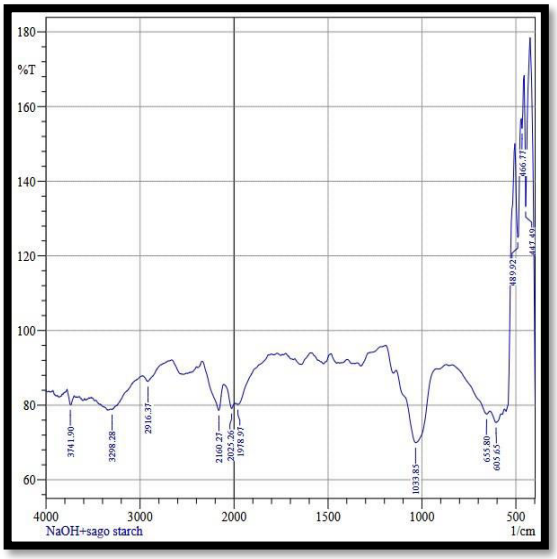

Figure 4: FTIR-NAOH+SS

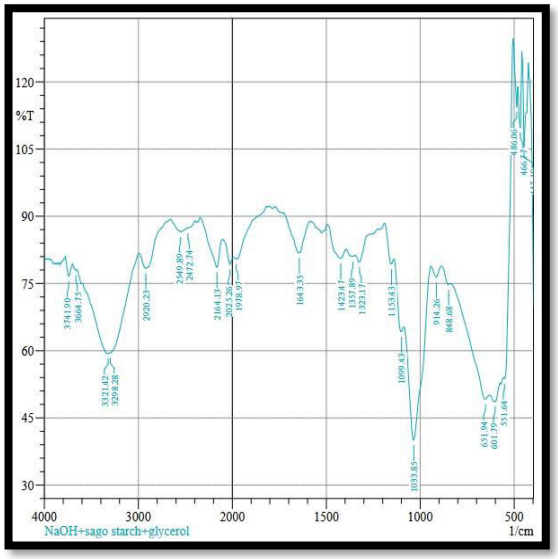

Figure 5: FTIR-NAOH+SS+GlY

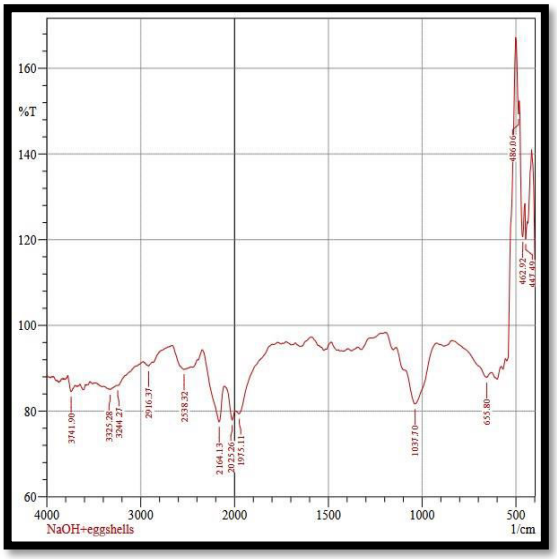

Figure 6: FTIR-NAOH+ ES

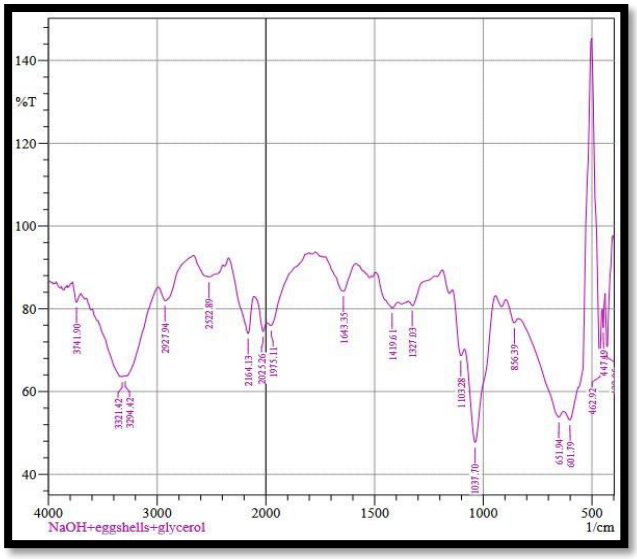

Figure 7: FTIR-NAOH+ES+GlY

3.4 SEM Analysis

The surface morphology of PALF samples were evaluated based on the SEM images shown in Figures 8 - 10. Heated pineapple leaves in NaOH solution breaks down non-cellulosic materials such as hemicellulose, lignin, waxes, fats and pectins, leaving behind mostly cellulose fibers. The untreated PALF surface exhibited a rough,fibrillated and porous surface. The fibers appeared loosely connected, with noticeable gaps and inconsistencies between them. These voids suggest weak fiber bonding and poor interfiber adhesion (Aghjeh et al., 2022). Figure 9 shows the SEM image of the sample with the addition of sago starch. The image shows enhanced bonding between fibers. Starch in heated water undergoes gelatinization, forming a sticly paste, which bind the pineapple fibers. Starch gelatinized around 60-80^{o}C, at which point the starch granules swell, and amylose leaches out, forming a gel-like network that functions as a natural binder. The starchfills the spaces between fibers and creating a denser, more uniform structure. Amylopectin, with its highly branched structure may remain within the granules and contribute to flexibility in the PALF. The surface appeared smoother and less porous compared to Figure 8, indicating improved cohesion. Similar findings were reported by Mahmud et al. (2023). While the addition of starch may increase stiffness, excessive starch can cause brittleness. Being hydrophilic, starch also increases the water absorption of the materials. The addition of glycerol resulting to smoother surface as shown in Figure 10. Glycerol acts as plasticizer, reducing the brittleness of the PALF. It improves interfacial bonding between fibers by forming smooth coating over the fibrils.

Replacing starch with eggshell powder alters the properties of PALF. While starch, an organic polymer, produces a pasty mixture that binds fibers, inorganic eggshells powder generates a more rigid structure. The eggshell particles act as a filler increasing the rigidity and brittleness of PLAF. As shown in Figure 11, the SEM image reveals visible eggshell particles embedded throughout the fiber matrix. These

particles appeared as irregular granules partially attached to the fiber surfaces. Although some microvoids remain, the eggshells contribute to the mechanical reinforcement of the structure. The absent of starch reduce the water absorption, but results in weaker fiber-particle adhesion. The addition glycerol coats the film, and imparts improved flexibility.

Overall, these findings show that the addition of sago starch and glycerol coating producesa uniform and compact morphology due to the gelatinization of the starch and binding effect of glycerol. The addition of eggshells contributes to structural support, although the surface remains slightly rougher without sufficient coating. Applying a glycerol-based coating improves surface smoothness and continuity. In the starch-coated sample, glycerol likely acts as a plasticizer, forming a thin, continuous film that seals the surface and minimizes microcracks and pores, thereby increasing flexibility. For the eggshell-coated sample, the glycerol coating helps reduce the surface unevenness caused by coarse particles, although it does not completely smooth the texture due to the rigidity of the eggshells. Nonetheless, both coated samples exhibited lower porosity and a more compact microstructure than their uncoated versions.

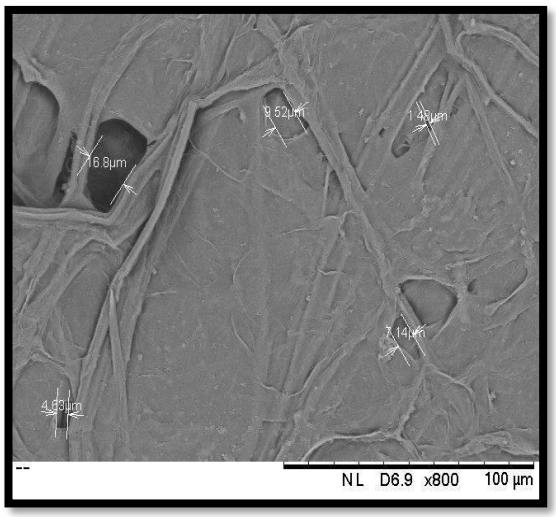

Figure 8: SEM-NAOH

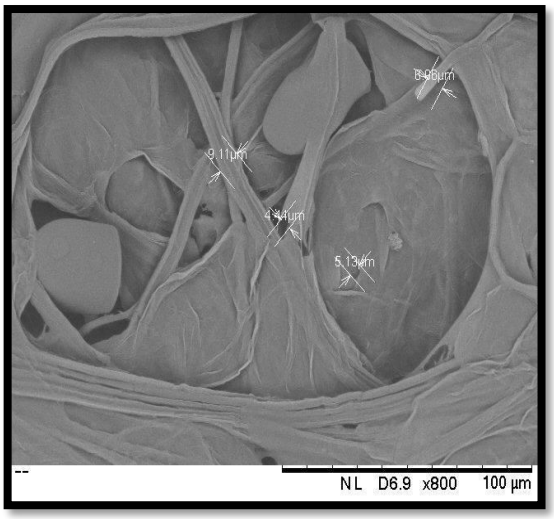

Figure 9: SEM-NAOH+SS

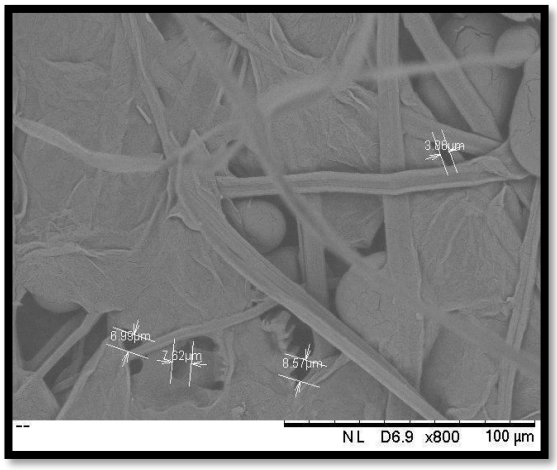

Figure 10: SEM-NaOH+SS+GlY

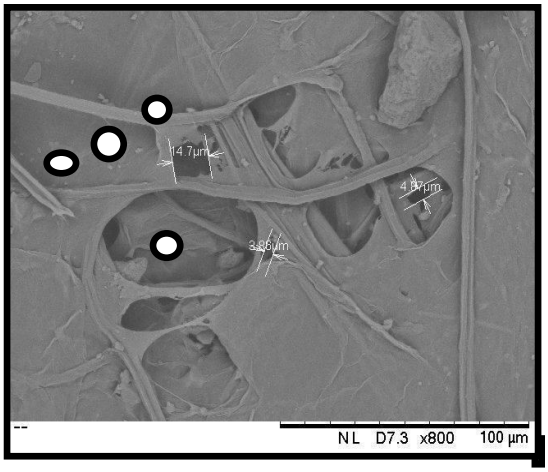

Figure 11: SEM-NAOH+ES

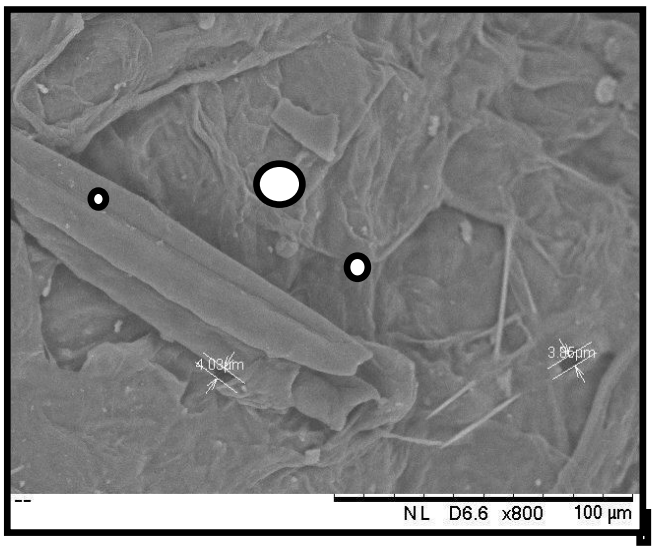

Figure 12: SEM-NAOH+ES+GlY

3.3 TG Analysis

Figures 13–17 show the TGA analysis for the pineapple leaf-based papers. In general, the TGA analysis demonstrates distinct thermal degradation phases as the temperature increases commonly found for lignocellulosic material. As shown in Figure 13, the PALF samples exhibit negligible mass loss, occurring between 25 °C and 150 °C, corresponds to the evaporation of physically bound moisture. This is followed by the decomposition of hemicellulose between 200 °C and 300 °C, which is less thermally stable and breaks down into volatile products, leading to a decline in sample mass. Significant mass loss occurs between 250 °C and 400 °C, where cellulose undergoes pyrolysis, resulting in the formation of gases, lowmolecular weight compounds and char. Lignin, in contrast, decomposes more slowly over a broader range of 200 °C to 500 °C due to its highly cross-linked and complex polymeric structure. Similar findings found by Esquivel-Alfaro et al., (2025) who studied on PALF, Laftah and Wan Abdul Rahman (2024) who studied PALF modified with corn starch and Nordin et al., (2018) who studied the thermal properties of starch films. Above 500 °C, the degradation process concludes with the formation of residual ash composed of inorganic minerals and carbonized remains Zhuang et al., (2025), with the final mass depending on the original composition of the material. The treatment of pineapple leaves with NaOH supposed to break down the hemicellulose and lignin, but there could be some of remained, which decomposed as shown in the TGA analysis here.

The TGA profile of the paper reinforced with eggshell shows noticeably enhanced thermal stability compared with the other samples. Minimal mass loss is observed below 100 °C, indicating reduced moisture absorption, as eggshell is inorganic and does not contribute to hygroscopic behavior. Although the main decomposition still occurs within the 200–400 °C region, the onset of degradation shifts slightly toward a higher temperature, and the mass-loss transition becomes broader and more gradual.

This reflects the stabilizing influence of the eggshell filler, which acts as a thermal barrier, slowing heat transfer and reducing the combustion rate of the organic matrix. The residue remaining after 450 °C is significantly higher than in the other papers, indicating greater non-combustible mineral content. This aligns with the high calcium carbonate content of eggshells, which increases char formation and improves resistance to complete thermal burnout. The DTA curve also shows a less pronounced exothermic peak, demonstrating that the presence of inorganic filler lowers the intensity of thermal oxidation reactions.

In contrast, the paper incorporating starch and glycerol exhibits higher mass loss below 100 °C due to greater moisture absorption, as both additives are hydrophilic plasticizers. Although the main degradation for all samples occurs between 200 °C and 400 °C, the composite containing starch and glycerol begins to degrade earlier and shows a broader mass-loss region. This indicates reduced thermal resistance, as starch and glycerol degrade at lower temperatures than cellulose and disrupt the hydrogen-bonded network within the fiber matrix. The DTA profile of this sample displays a more gradual and diffuse thermal response compared with the NaOH-only sheet, reflecting overlapping decomposition of multiple components. The final char residue is also lower than in the eggshell-reinforced sample, as glycerol volatilizes completely and does not contribute to inorganic ash. Overall, the TGA results confirm that glycerol acts as a plasticizer that improves flexibility and processability of the paper but reduces thermal stability and shifts the decomposition reactions to lower temperatures.

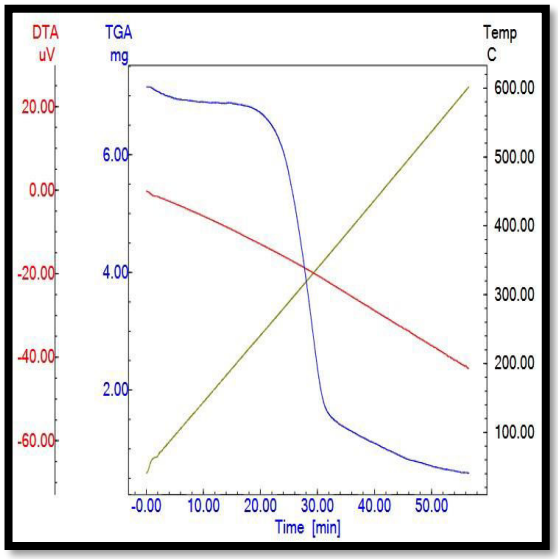

Figure 13: TGA-NAOH

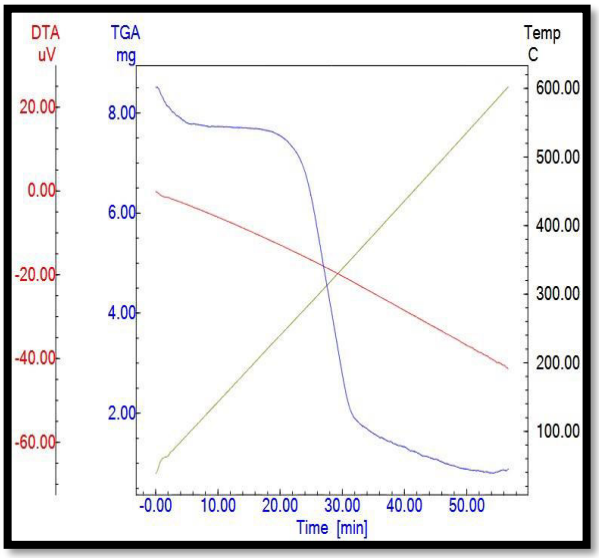

Figure 14: TGA-NAOH+SS

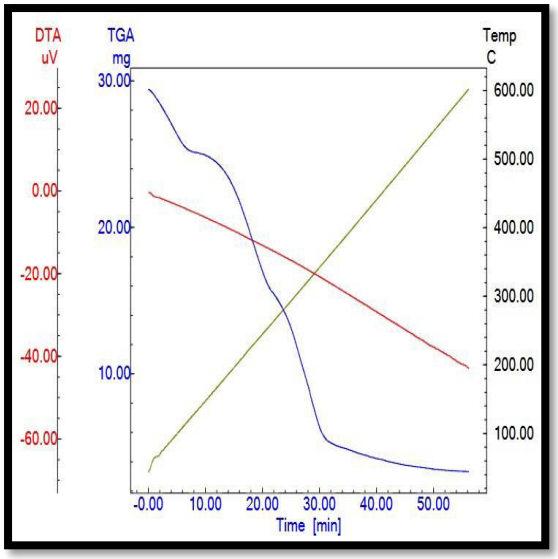

Figure 15: TGA-NAOH+SS+GlY

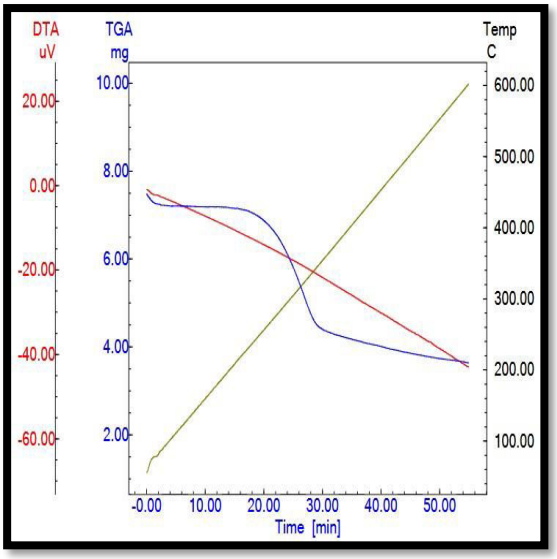

Figure 16: TGA-NAOH+ES

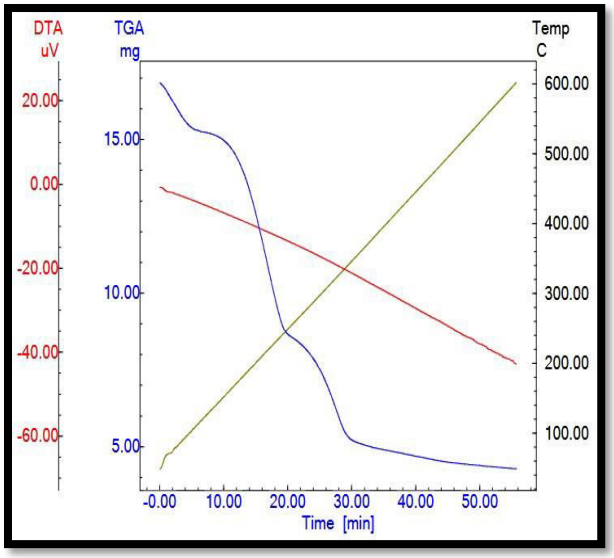

Figure 17: TGA-NAOH+ES+GlY

4. Conclusion

The comprehensive analysis of pineapple leaf fibre (PALF) demonstrates its strong potential as an eco-friendly material for paper-based food packaging. Pulping results showed that a cooking time of 90 minutes is optimal, achieving complete fibre breakdown and producing a smooth, uniform paper structure. FTIR analysis verified effective successful incorporation of starch, glycerol, and eggshell powder, each influencing the chemical environment of the composite. SEM images further illustrated the role of additives in modifying surface morphology, starch enhanced fibre bonding, eggshell powder increased rigidity and structural reinforcement, while glycerol improved flexibility through plasticization.Thermal degradation studies indicated that NaOH-only fibres exhibit good stability, but eggshell-reinforced samples offer superior heat resistance and the highest residual mass, suggesting the incorporation of inorganic such as eggshell enhance the suitabilityof the paper for hot

and oily food applications. In contrast, glycerol-containing composites showed reduced thermal stability and therefore limited applicability in high-temperature conditions. Collectively, the results show that PALF combined with eggshell powder and without glycerolprovides the best performance in terms of thermal endurance, rigidity, barrier properties, and overall structural integrity.Thus, PALF–eggshell composite paper emerges as a promising biodegradable packaging material capable of reducing dependence on petroleum-based plastics while fulfilling functional requirements for sustainable food packaging.

5. Acknowledgement

The authors thank Universiti Malaysia Sarawak for providing the materials and laboratory facilities. Thank you also due to the research assistants, Airul Azhar bin Jitai and Dayang Fadhilatul Aishah binti Abang Abdul Hamid.

6. References

1. Aghjeh, M. K. R., & Razavi, M. J (2022). Effect of interfibre bonding on mechanical behaviour of electrospun fibrous mats. Mechanics of Fibrous Networks,317-354.
2. Chaves, D.M., Fangueiro, R., Araújo, J.C., Ferreira, D.P (2024). Extraction, characterization and properties evaluation of pineapple leaf fibers from Azores pineapple, Heliyon, e26698.
3. Chamas, A., Moon, H., Zheng, J., Qiu, Y., Tabassum, T., Jang, J.H., Abu-Omar. M., Scott, S.L. and Suh, S (2020). Degradation rates of plastics in the environment. Sustainable Chemistry & Engineering, 8: 3494-3511.
4. Fayshal, M. A., Dhara, F. T., Hasan, M. M., Adnan, H.M.F. and Tahiat, M (2023). Global plastic waste scenario: a review on production, fate and future prospects. Proceedings of the Waste Safe 2023, 8th International Conference on Integrated Solid Waste and Faecal Sludge Management, 25-26 February 2023, Khulna, Bangladesh.
5. Kengkhetkit N, Amornsakchai T (2014) A new approach to“Greening” plastic composites using pineapple leaf waste for performance and cost effectiveness. Material & Design, 55:292–299.
6. Laftah, W. A. and Wan Abdul Rahman, W.A (2024). Chemical surface modification of pineapple leaf fiber for polymer composites applications: Comparative study, Polymer and Polymer Composites, 32:1-7.
7. Liang, Y., Tan, Q., Song, Q., Li, J (2021). An analysis of the plastic waste trade and management in Asia.Waste Management,119:242–253.
8. Mahmud, M. A., Belal, S. A., & Gafur, M. A (2023). Development of a biocomposite material using sugarcane bagasse and modified starch for packaging purposes. Journal of Materials Research and Technology, 24:1856-1874.
9. McMurry, J.E (2012). Organic Chemistry. Mary Finch, 424-448.
10. Mwaikambo, L (2006). Review of the history, properties and application of plant fibres. African Journal of Science and Technology, 7:120-133.

11. Nordin, N., Othman, S.H., Kadir Basha, R. and Abdul Rashid, S (2018).Mechanical and thermal properties of starch films reinforced with microcellulose fibres. Food Research, 2(6):555-563.
12. Ncube, L.K., Ude, A.U., Ogunmuyiwa, E.N., Zulkifli, R. and Beas, I.N(2021). An overview of plastic waste generation and management in food packaging industries. Recycling, 6(1): 12.
13. Pilapitiya, P.G.C.N.T and Ratnayake, A.S (2024). The world of plastic waste: A review. Cleaner Materials, 100220.
14. Siregar, J.P., Salit, M.S., Ab. Rahman, M.Z. and Mohd. Dahlan, K.Z (2011) Thermogravimetric analysis (TGA) and differential scanning calometric (DSC) analysis of pineapple leaf fibre (PALF) reinforced high impact polystyrene (HIPS) composites. Pertanika Journal of Science and Technology, 19 (1): 161 – 170.
15. Tanpichai, S. and Witayakran, S (2017). All-cellulose composite laminates prepared from pineapple leaf fibers treated with steam explosion and alkaline treatment, Journal of Reinforced Plastics &Composites, 36(16):1146-1155.
16. Tran, T.V., Nguyen, D.T.C., Nguyen, T.T.T., Nguyen, D.H., Alhassan, M., Jalil, A.A., Nabgan, W. and Lee, T (2023). A critical review on pineapple (Ananas comosus) wastes for water treatment, challenges and future prospects towards circular economy. Science of the Total Environment, 856:158817.
17. Saini, R., Singhania, R.R., Chen, C.W., Patel, A.K., Saini, J.K., Chauhan, A.S. and Dong, A.D (2023). Pineapple leaves waste — a potential feedstock for production of value-added products in biorefinery. Indian Journal of Experimental Biology, 61:729-738.
18. Yang, H., et al. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel, 86(12–13):1781–1788.
19. Vagenas, N.V., Gatsouli, A. and Kontoyannis, C.G (2003). Quantitative analysis of synthetic calcium carbonate polymorphs using FT-IR spectroscopy. Talanta, 59: 831-836.
20. Esquivel-Alfaro, M., Sulbarán-Range, B., Rojas-Carrillo, O., Chen, J., Rodríguez-Quesada, L., Sáenz-Arce, G. and Rojas, O.J (2025). Processing of pineapple leaf fibers for the production of oxidized micro-/nanofibrillated cellulose.Polymers, 17:2671.
21. Zhuang, D., Chen, Z. and Sun, B (2025). Thermal decomposition of calcium carbonate at multiple heating rates in different atmospheres using the techniques of TG, DTG, and DSC. Crystals, 15:108.