KESUM *(POLYGONUM MINUS)* FIBER BIOCOMPOSITE: EFFECT OF ALKALI TREATMENT ON THE TENSILE, MORPHOLOGICAL AND THERMAL PROPERTIES

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ABSTRACT

In Malaysia, *Polygonum minus* (Polygonaceae), often known as 'kesum,' is one of the most widely used food additives, flavoring agents, and traditional pain relievers. The primary purpose of this study is to compare the interfacial adhesion qualities of untreated Kesum fiber with alkali-treated Kesum fiber impregnated in Polylactic Acid (PLA) for PLA/Kesum biocomposite active packaging and manufacture utilizing the Solution Casting technique. The mechanical, morphological, and thermal properties of the bio-composite have been compared to those of PLA. Good interfacial bonding between fiber and matrix increases the tensile properties of composite material by increasing the frictional resistance against tensile loading in alkali-treated samples, as indicated by the mechanical properties. A SEM image demonstrated that PLA with alkali-treated Kesum exhibits enhanced stress transmission between the matrix and fibers. The mechanical properties of PLA/Kesum bio-composites will be enhanced by a good stress transfer of fiber-matrix due to a better fiber-matrix adhesion. In addition to the good miscibility of PLA with untreated kesum fiber, thermal investigations conducted on these samples demonstrate the superior thermal stability of PLA with alkali-treated Kesum at a higher decomposition temperature.

Keywords: *kesum, bio-composites, active packaging, solution casting*

1.0 INTRODUCTION

As people become more conscientious of the environment, they are demanding more and more ready-to-eat disposable meals that can be recycled or composted, thus reducing their impact on the environment. Growing efforts in the field of packaging research have aimed to introduce and popularize the usage of biocomposite in creating a secure and biodegradable food packaging. Biocomposite, formed by combining matrix and fiber, can enhance the features of food packaging. Matrix and fiber play important roles in biocomposite food packaging, contributing to its overall qualities in their own ways [1]. Biodegradable and compostable bioplastics can be made from conventional plastics, making them suitable for use in food packaging without posing any health risks.

An example of a bio-based and biodegradable polymer used for food packaging is polylactic acid (PLA). Synthetic lactic acid is produced through the fermentation of sustainable agricultural raw materials like corn starch or sugar cane. Bacterial fermentation is used in industrial production of lactic acid from a wide variety of substrates, including corn, potato, beet, cane sugar, dairy products, and even agricultural waste [2].

Figure 1: Kesum plant

Since bio-plastics are both biodegradable and biocompatible, they have attracted a lot of interest for use in food packaging. This is because of their potential applications in the fields of medicine and biotechnology. While the primary purpose of food packaging is to prevent the spread of disease by preventing the growth of microorganisms, it also serves as a retainer, keeping foods at their peak of freshness and quality. The intended packaging needs to be naturally biodegradable to prevent pollution during disposal, and it needs to be inexpensive for the average consumer. Food safety, which is dependent on the structure of polymeric packaging materials, necessitates careful management and modification of the mechanical and barrier properties of bio-plastic materials[3]. Bio-plastics' properties can be seen changing during interaction time with food to ensure the quality of the meal is not compromised.

Cellulose, hemicellulose, and lignin are the three primary components of natural fibers. Cellulose makes up 60–80% of natural fibers, lignin makes up 5-20%, and moisture makes up to 20% [4]. Cellulose serves a functional purpose in that it mechanically reinforces the fiber. Hemicellulose molecules, meanwhile, will serve as hydrogen bonds between the cellulose molecules.

Known as kesum in Malay, *Polygonum minus* is highly prized for its unique flavor. Both the leaves and the stems have been used extensively in cooking and as a folk remedy for many ailments. Countries in Southeast Asia like Malaysia, Indonesia, Thailand, and Vietnam are good sources for this plant [5]. The kesum used in this study is depicted in Figure 1. Kesum, thanks to the aliphatic aldehydes contained in the essential oil it produces (72.54%), is an aromatic plant, contain a flavor derived in part from the presence of two major aldehydes, specifically decanal (24.36%) and dodecanal (48.18%) [6]. Kesum's natural source of aliphatic aldehydes brings tremendous advantage to all disciplines, therefore it's been used in a wide variety of businesses, from food additives to the perfume industry.

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This research makes use of the solution casting method to create bio-composite material with kesum fiber as a filler. The quality and characterisation of the finished product can be figured out by testing its properties and going through the characterization process.

2.0 METHODOLOGY

Multiple procedures, including drying and grinding, have been performed on kesum fiber. Then, a thin layer of PLA/Kesum biocomposite was made using a solution casting approach, which involved combining PLA and Kesum fibre. The research process, depicted as a flowchart in Figure 2, has been presented here. Using an oven set to 70°C for 1 hour, a commercial grade PLA 4042D matrix from NatureWorks was dried out before the next stage of sample preparation was taken. The kesum leaves used in this preparation were purchased at a local market, thoroughly cleaned, the leaves removed from the stems, and then dried in an oven at 70°C for 24 hours. The leaves were dried, then pulverized in a high-speed grinder, and finally sieved at 250 m.

2.1 Alkali Treatment of Kesum Fibre

Kesum fibre was treated by soaking it in a 5wt% NaOH solution for 1 hour at 25°C. After that, the fibers were handed a thorough soaking in distilled water to get rid of any remaining NaOH solution. In order to eliminate of the remaining moisture in the alkali-treated Kesum fiber, the fibers were dried in an oven at 70°C for 24 hours.

2.2 Preparation of PLA Biocomposite Film via Solution Casting

The PLA pellets were dissolved in chloroform inside a beaker. Kesum particles were mixed at a concentration of 3wt% in the beaker. Each sample contained a weight of 5g of PLA and Kesum fiber. Chloroform was raised to a 50ml concentration. After that, a magnetic stirrer was used to agitate the liquid for 2 hours at a speed of 4-5fpm. To eliminate air bubbles in the sample, the chloroform must be stirred constantly until the PLA pellets and Kesum powder are completely dissolved. Dissolved ingredients were then poured into the flat-bottomed mold. To expedite the drying process, samples were left out at room temperature for a whole day. Using both treated and untreated fiber, the same processes were carried out again to create a film of PLA biocomposite.

Shimadzu Autograph AGS-X series universal material testing equipment was used to conduct tensile tests on untreated and alkali-treated fiber PLA biocomposite film according to the American standard ASTM: D882. To investigate the fractured fibre-matrix interface and surface morphology, and microscopic examinations SEM characterization were performed using a JSM-IT100 InTouchScope Scanning Electron Microscope. ATR sampling was used to capture 45 scans in transmission (%) mode between 4000-400 cm^{-1} of the IR spectra of both untreated and alkali treated fiber PLA biocomposite film using a Bruker TENSOR 27 FTIR spectrophotometer. Finally, thermal gravimetric analysis (TGA) was performed on the biocomposite film according to the American standard ASTM: E1131. TA Instrument's Q500 thermogravimetric analysis machine was used to record the thermograms of the samples. After conducting mechanical, morphological, and thermal testing on PLA/Kesum biocomposite films, this study was concluded.

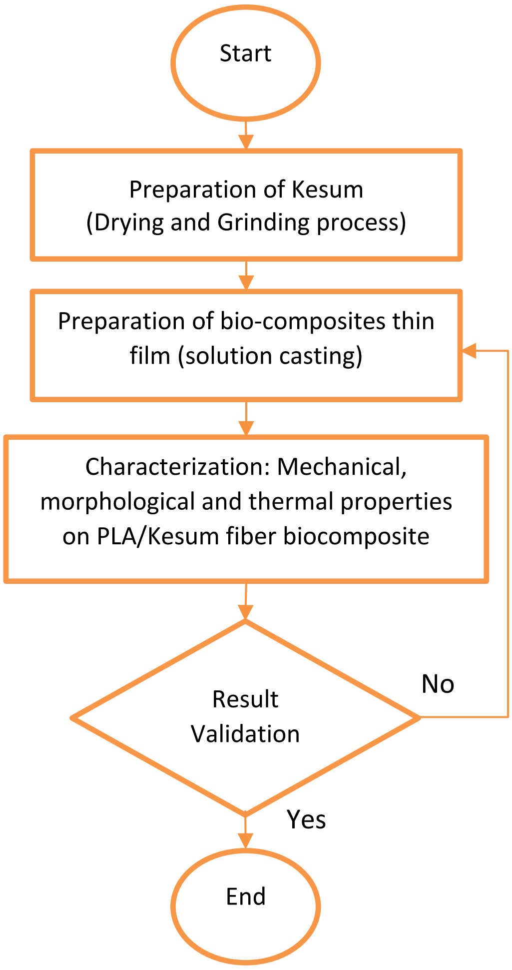

Figure 2: Flowchart of the methodology

3.0 RESULTS AND DISCUSSION

As fibre qualities may affect the properties of biocomposites, a study of fibre properties is necessary to understand the interaction between fibre and matrix, as well as their bonding within composite materials. When matrix and fiber are combined, this interaction influences the mechanically enhanced properties of the biocomposites, or vice versa.

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3.1 Tensile Properties

To analyze the tensile behaviour, the typical stress-strain of PLA, PLA/Kesum treated and untreated samples is observed. PLA/Kesum that has been treated has the maximum tensile strength and fracture strain. The elastic area of PLA, treated PLA/Kesum, and untreated PLA/Kesum is represented by the graph's curve in Figure 3, when a quick increase in stress precedes plastic deformation. Matrix and interface cracking will occur during plastic deformation, leading to the ultimate breakdown of the composite system. At this point, the fibre-matrix interface will begin to detach. The fiber will pass the imparted stress to the matrix to prevent it from cracking at the fracture site. This crack widens, which increases the strain placed on the connecting fiber. When the stress of fibre bridging reaches the critical level, it can produce fibre and composite fractures. Removing covering layers such as lignin and hemicellulose is believed to improve the fibre surface by promoting strong fibre-matrix interfacial adhesion. This will postpone the cessation of stress transfer within the composite, as the debonding process at the fibre-matrix interface was interrupted. When the fibre-matrix begins to debond and matrix cracking propagates, the overall strength and stiffness of the composite will drop [2]. Consequently, a strong interfacial bond between the fibre and matrix can enhance the tensile characteristics of composite materials by increasing the frictional resistance against tensile loading.

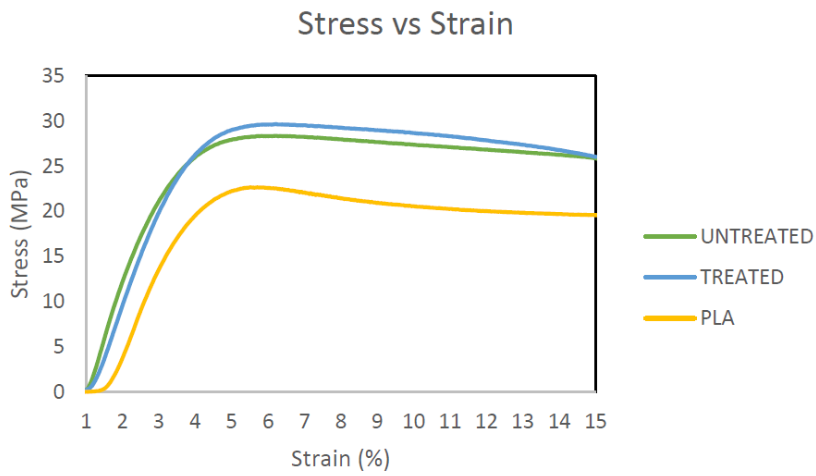

Figure 3: Typical stress-strain curve of fibre composite

3.2 SEM Observation

Figure 4 depicts the comparable SEM images of these thin films. On the basis of the observed microstructure, it can be seen that the surface of the untreated Kesum-reinforced PLA composite exhibits significant fibre pull-out. This is owing to inadequate adhesion between the fibre and matrix, as holes on the surface indicate that the fibre has been pulled out. There is a noticeable separation between fiber and PLA matrix. The pulled-out fibre includes no traces of attached matrix because matrix and fibre compatibility is diminished, resulting in the quick partial collapse of PLA composite. As a result of treating the surface of the fiber with alkali, the voids vanished. During crack propagation, the Kesum-reinforced PLA composite treated with alkali exhibited the features of fibre breakage rather than pull-out, demonstrating its strong compatibility with the fibre matrix. This suggests that PLA containing Kesum that has been alkali-treated has a more efficient stress transmission between the matrix and fibres. The mechanical characteristics of PLA/Kesum biocomposites would be enhanced by a good stress transfer of fibre-matrix due to improved fibre-matrix adhesion.

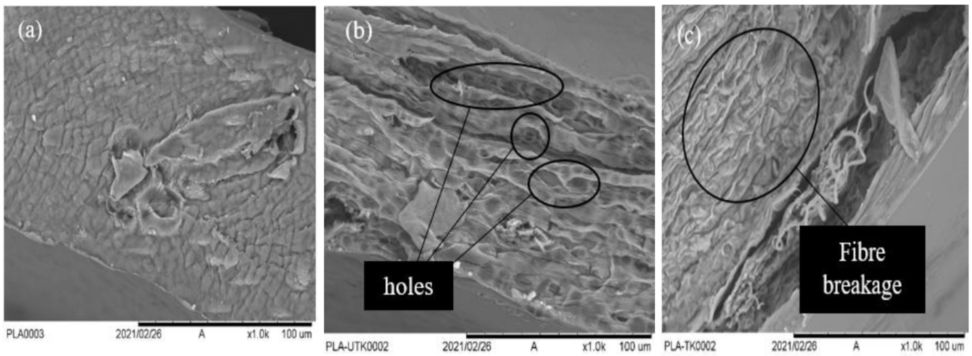

Figure 4: SEM image of (a) PLA, (b) PLA with untreated Kesum and (c) PLA with alkali-treated Kesum at the fractured surface

3.3 FTIR Analysis

Infrared spectroscopy was used to study the effect of alkali treatment on Kesum. Figure 5 presents the infrared spectra of PLA, PLA with treated Kesum, and untreated PLA. Analyses of the results reveal that amorphous portions of the fiber dissolve when treated with NaOH solution in an alkaline environment. CH group peaks were identified between 3000 and 2800 cm-1, and this band exhibited a higher absorption of PLA with treated Kesum than PLA and PLA with untreated Kesum. This is anticipated to occur as the presence of PLA will lead to the formation of -CH2- and –CH groups. At 1700 cm-1, the carbonyl stretching absorption band is observed in these thin films composed of PLA, PLA with treated and untreated Kesum, which correspond to hemicellulose. Due to the presence of an aromatic or benzene ring in lignin, absorption within the range of 1600-1400 cm-1 can be observed in the composite spectrum. At 1400-1300 cm-1, the spectra revealed the aliphatic or aromatic (C-H) in plane deformation vibration of methyl and methoxy groups in fiber. Le et al. 2017 state that the C-O stretching vibration of aliphatic primary and secondary alcohols in lignin, cellulose, and hemicellulose, as well as primary and secondary aromatic alcohols in lignin, may be observed in the spectra with a peak at 1300-1100 cm-1. During surface treatment, the alkaline solution removes the waxy layer, hemicellulose, and sticky pectins from the fibre surface, therefore there is no absorption peak at 1245 cm-1 for PLA with treated Kesum. As a result, it was discovered that the fiber was linked together. At 1100 cm-1, the C-O-C symmetry glycocidic

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of polysaccharide components, which were mostly cellulose, was stretched. This absorption band is more likely to be present in the spectra of treated and untreated fibre composite systems as compared to PLA single systems.

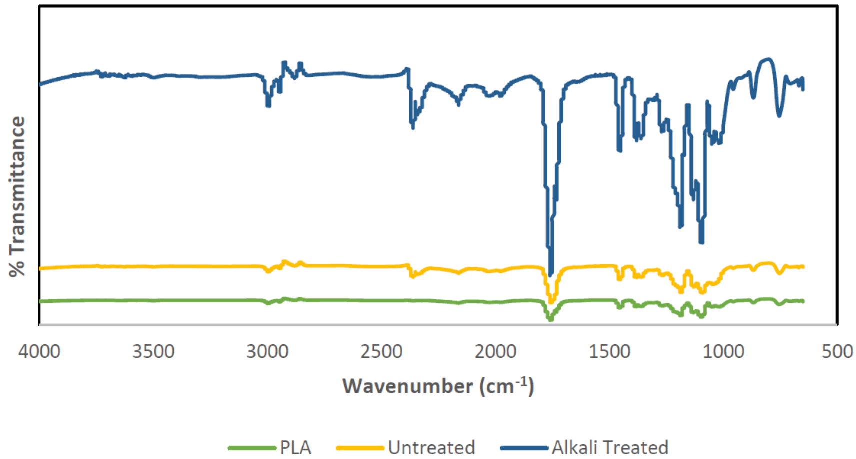

Figure 5: Infrared spectra for the PLA, PLA with treated and untreated Kesum

3.4 Thermogravimetric Analysis

TGA is used to examine the changes in mass, thermal stability, and thermal degradation of materials by displaying a temperature-dependent curve. According to Debeli et al. 2018, statistical chain breakage produces a substantial deterioration stage for PLA composites between 360°C and 400°C. Other researchers have determined that the maximal breakdown temperature for PLA composites is between 350°C and 400°C. By analyzing the thermal breakdown at the start and ultimate weight loss of PLA as well as untreated and alkali-treated PLA/Kesum biocomposites, the improvement in thermal stability of Kesum fiber after alkali treatment can be analyzed. The TGA curve displays the breakdown temperatures of PLA, untreated PLA/Kesum, and alkali-treated PLA/Kesum biocomposites, as shown in Figure 6.

It can be noted that the PLA breakdown process began at 315°C and concluded at 385°C. Initial and final readings of deterioration temperature for the untreated PLA/Kesum were 307°C and 380°C, respectively, whereas the alkali-treated PLA/Kesum showed readings of 300°C for initial degradation temperature and 375°C for ultimate degradation temperature. The polymer has a higher onset temperature than lignocellulose materials, but a negligible mass residual after testing [9]. It indicates that PLA is thermally stable. Because additional heat was applied to PLA, the relatively lengthy molecular chain was broken. The addition of natural fiber will improve the mobility of PLA's molecular chains, causing some of the chains to breakdown and form crystals. This reduces thermal deterioration caused by the production of crystals during the plasticization and heterogeneous nucleation processes [10].

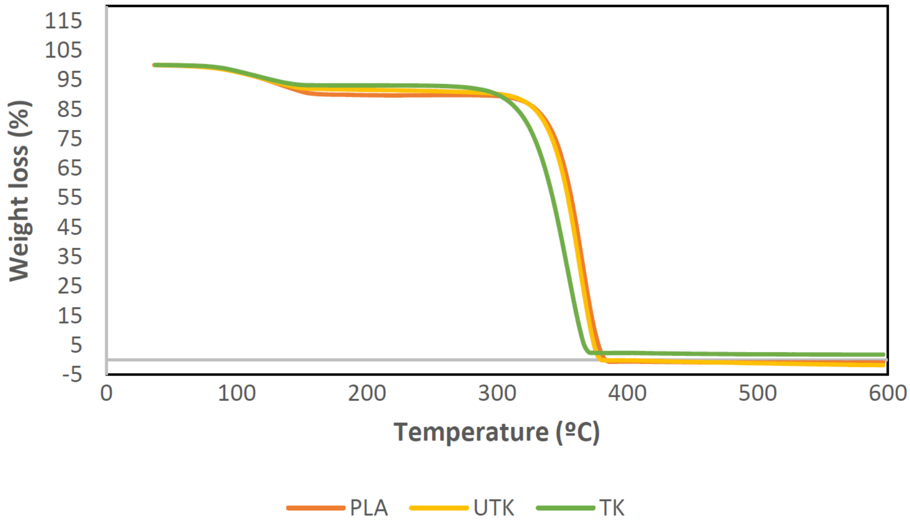

Figure 6: TGA curve of PLA, untreated and alkali-treated PLA/Kesum

As lignocellulose decomposes at an earlier stage than PLA/Kesum, materials containing lignocellulose may have less heat stability. The three primary components of kesum fibre are cellulose, hemicellulose, and lignin. As the fibre degrades thermally during the production process, the PLA/Kesum biocomposite has a lower decomposition temperature than PLA. As the deterioration rate of PLA crystals increases, the thermal stability of the composite decreases as well. Incorporating natural fiber with PLA will lower PLA's thermal stability, as less thermally stable natural fibers, such as Kesum leaves, have already supplanted certain PLA. In addition, when the relative molecular mass of PLA decreases, the thermal stability of composites may decline. This finding can be confirmed if the similar trend is observed in PP-filled OPEFB fiber composites, as reported by [11].

The graph in Figure 6 reveals that the TG curve of alkali-treated PLA/Kesum biocomposites rapidly decreases in comparison to untreated PLA/Kesum biocomposites. This can be explained by the alkalization process, which may damage the cellulose structure while removing lignin from the fibre surface, resulting in a rapid degradation of the material. Crystallinity index of treated composites also influences degradation, with a low crystallinity index increasing the rate of degradation and decreasing the thermal stability of the material. In addition, the percentage of PLA residue differs between untreated and alkaline-treated PLA/Kesum biocomposites. It can be seen that the untreated composite produced the greatest residues, while PLA produced the least. As a result of the presence of Kesum fibre as a reinforcement in the composite system, PLA/Kesum composites have a higher heat resistance than PLA. In compared to PLA/Kesum that has been treated with alkali, untreated PLA/Kesum exhibits superior heat resistance.

4.0 CONCLUSION

The major purpose of this study is to develop biocomposite materials that can be utilized as active packaging through the development of bio-based composite materials. Kesum fiber, the primary filler ingredient for this bio-composite sheet, is alkaline-treated to enhance its strength and optimize its thermal properties. In this study, thin films made of treated PLA-kesum were cast using a solvent casting approach, and their mechanical properties were comparable to those of previously obtained thin films. In addition, it was discovered that this PLA/Kesum thin film may perform well even when subjected to a wide range of temperatures. Overall, the research confirmed that kesum fiber and PLA might be used to create eco-friendly, renewable, and sustainable products.

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