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Utilization of Kiwi Peel Lignocellulose as Fillers in Poly(Lactic Acid) Films

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Abstract: Lignocellulosic structures extracted from agricultural wastes have great potential in re-designing sustainable packaging materials. In this study, the utilization of kiwifruit peels (KFP) (unt) and lignocellulosic structures extracted from KFP, which were alkali-treated (al), acid-treated (ac), and acetylated (ace), in poly(lactic acid) (PLA) films were investigated. Untreated and treated lignocellulosic structures were added to PLA film-forming solutions at 5% (w/w based on PLA). The film samples were characterized by their mechanical, water vapor permeability (WVP), FTIR, and optical properties. FTIR results presented that the acid treatment and acetylation have changed the chemical structure of KPF, which resulted in changes in intensities and peak shifts between 1400-1900 cm^{-1}. WVP of the films containing KPF-based lignocellulosic structures was lower than control PLA films ($p<0.05$). The addition of KPF-based lignocellulosic structures increased the tensile strength and elastic modulus ($p>0.05$) compared to PLA control films. Films including acid-treated lignocellulosic structures had high opacity and relatively low lightness values ($p<0.05$). These results showed that adding lignocellulosic structures into PLA films is a promising method to improve the film properties.

Keywords: Kiwifruit peels, Lignocellulose, Modification, Poly(lactic acid)

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INTRODUCTION

The rise in energy demand, the increase in carbon gas emissions, and the depletion of fossil-based sources have recently raised environmental concerns (1,2). The circular economy promotes the transition from petroleum-based materials to renewable materials and greener processes for obtaining energy and materials. Biowastes are an abundant and inexpensive source. Their complete utilization to extract added-value materials is an appealing option from an eco-friendly standpoint (2–5). Among the various biomasses, lignocellulosic biomass accounts for nearly 70% of total plant biomass (4). Thus, the environmental problems and depletion of fossil resources have increased interest in green and sustainable chemistry, which focuses on lignocellulose-based materials as a promising, abundant, and renewable resource for different materials (6–8). The main constituents found in lignocellulosic structures are cellulose (homopolymer), hemicelluloses (heteropolymer), and lignin (aromatic polymers) (7–9). To convert them into various bio-based compounds, individual fractions could be recovered from lignocellulosic biomass (10).

Researchers have used pre-treatments to separate these main structures (lignin, hemicellulose) from lignocellulosic structures, modify, improve their reactivity by extracting those valuable constituents, and change degrees of crystallization and polymerization (11–15). Alkaline or acid hydrolysis has been widely used as a chemical pretreatment technique (16,17). Among the various pretreatments, alkaline de-lignification destroys the lignin structure and breaks linkages between lignin and carbohydrate to make the latter more accessible (18). Hydrothermal treatments are high-capacity treatments for hemicellulose solubilization while also producing cellulose and lignin-rich structures that are open to being treated to extract these components (19,20). Besides, acetylation has been used to plasticize the cellulosic fibers, substituting hydroxyl groups with acetyl groups to make the material more hydrophobic, stabilize the material against water, and enhance the degradation and stability (21). Ozone treatment is another biomass pretreatment method in which it oxidizes the structure to remove lignin and hemicellulose (22).

The use of lignocellulosic structures as fillers for bio-based polymers has gained popularity due to their better mechanical strength, wide range of availability, and being suitable for various chemical structure-based modifications (23–28). Many studies have examined the incorporation of agro-wastes into natural biopolymers such as starch, protein, cellulose, poly(lactic) acid (PLA), and polyhydroxy butyrate (PHB) to create bio-based plastics (23,26,29–31). Among biopolymers, PLA has been vastly studied due to its easily processed structure, having similar characteristics to conventional plastics, intrinsic biodegradability and biocompatibility, compostability, thermoplastic nature, and outstanding mechanical performance (32). However, to widen the application of PLA-based materials, PLA has been studied to modify its structure by various alternative methods such as blending with other polymers, reactive extrusion, using crosslinking agents or chain extender, chemical or physical modifications, and use of reinforcing agents including inorganic fillers and natural fibers (33–36). Among these applications, the addition of lignocellulosic structures such as corncob (37), yerba mate (32,38), bamboo, switchgrass (39), nanofibers from lignocellulose biomass (40) into PLA has also been gained attention by researchers.

Fruit peels, such as kiwifruit peels, are from the agro-food industry with promising potential as an appropriate raw material for use in a biorefinery (7). Kiwifruit processing creates wastes with bio-active properties of various sectors such as cosmetic, food, and pharmaceutical industries due to their bioactive molecules having health-promoting properties (41–44). After extracting active compounds (kaempferol and quercetin derivatives) from kiwifruit peel, the obtained solid fraction is primarily composed of lignocellulosic structures (45). Incorporating lignocellulosic structures obtained from agro-wastes like kiwifruit peel as reinforcements typically lowers cost and water uptake while increasing mechanical strength (46). Arrieta et al. (38) studied the effect of lignocellulosic-based mate nanoparticles extracted from yerba mate residue on the properties of PLA films. They reported enhanced thermal stability, increased flexibility, processability, UV light blocking effect, and an appropriate disintegration in compost. However, interfacial adhesion between PLA and natural fibers extracted from agro-wastes is one of the most important issues (37). Generally, weak interaction between PLA and lignocellulosic structures has been reported in the literature (47–49). Thus, research on the addition of modified lignocellulosic structures to improve the adhesion in thermoplastics/lignocellulose composites are gaining interest.

The food industry has been commercializing the kiwi fruit in diverse processed forms, even though the kiwi fruit is commonly consumed as fresh (50). Therefore, the byproducts such as the peel of kiwi fruit have been increasing and are still under-explored (51). However, a great interest in these byproducts has increased due to their high concentration of bioactive molecules (52). The characterization of kiwi fruit byproducts has been studied by many researchers (51); however, the valorization of these byproducts as fillers in biopolymers is required more studies to confirm their utilization. Besides, it has been reported that the direct use of these fillers might result in incompatibility problems, which chemical modifications on lignocellulosic structures could recover. PLA reinforcement with various chemically modified lignocellulosic fibers has been rarely studied. Thus, this study aimed to examine the valorization of kiwifruit peels in PLA films as fillers followed by different pre-treatments including alkali, acetylation, and acid treatments, and further evaluate regarding mechanical, water vapor permeability (WVP), Fourier transform infrared spectroscopy (FTIR), and optical properties, whether to determine the potential of kiwifruits byproduct in the food packaging applications.

MATERIALS AND METHODS

Materials

Kiwi fruits (KF) were provided from a local producer in Isparta (Turkey) and peeled to collect kiwi fruit peels (KFP). KFPs were then dried at 60 °C for 24 h and ground with a high-speed blender. After screening the obtained particles with suitable meshes, particles smaller than 300 µm in size were used in the experiments. Homogenized KFPs were coded as "unt" and stored at 4°C until use. Poly(lactic acid) (PLA) (4032D; molecular weight of 80,000-100,000 g/mol, 1.25 g/cm^3 of specific gravity, melt flow index of 5.89 g/10 min) was from NatureWorks LLC (Minnetonka, MN, USA) and other chemicals including sulfuric acid (H_2SO_4), ethanol, sodium hydroxide (NaOH), chloroform, glacial acetic acid, and magnesium nitrate ($Mg(NO_3)_2$) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA).

Extraction of Cellulose-Rich Structures from Kiwi Peels and Characterization

The extraction steps of cellulose-rich structures from KFPs are shown in Figure 1.

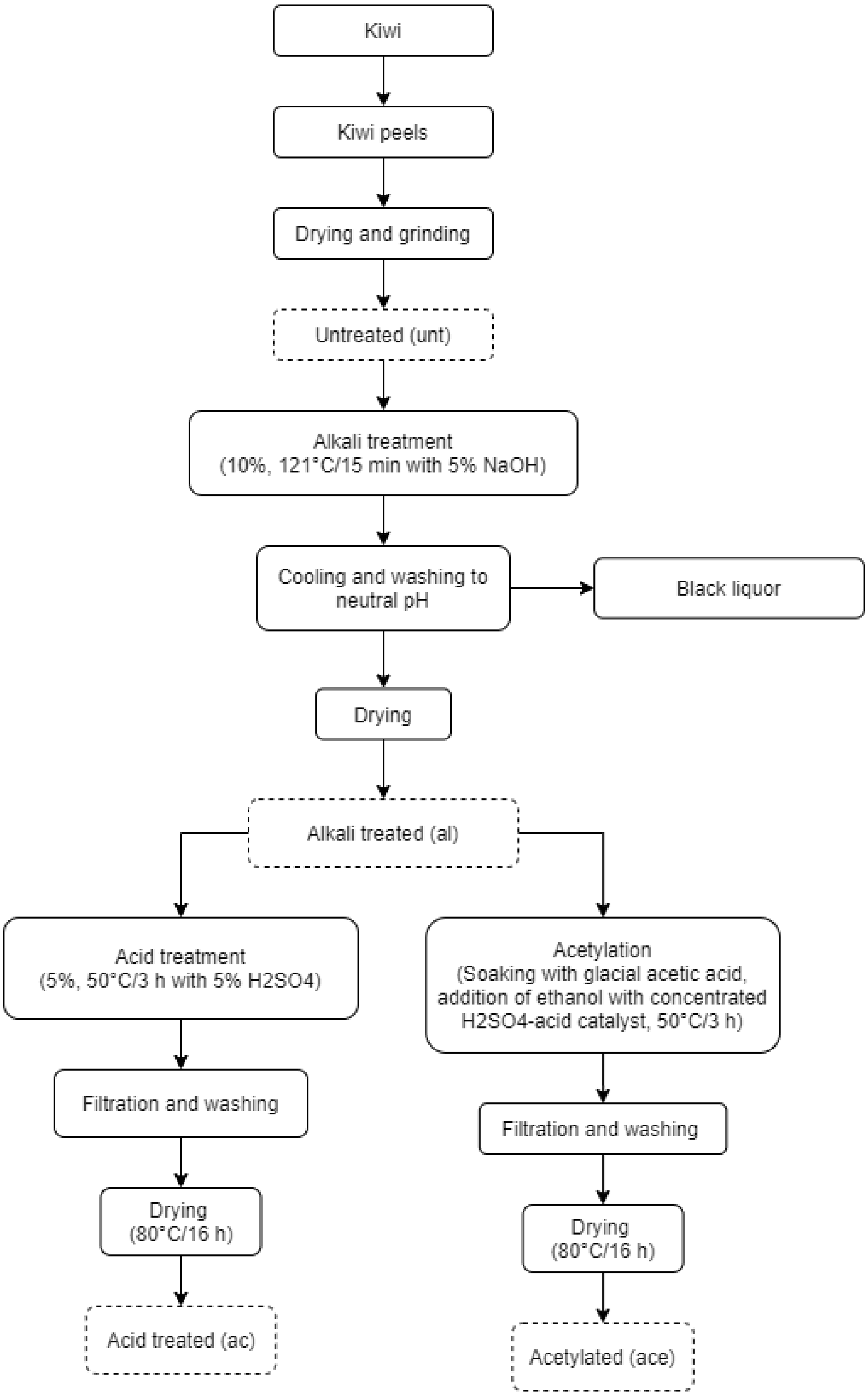

Figure 1: Schematic representation of extraction steps.

KFPs were de-lignified in an alkaline medium using NaOH at 5% (w/w) with a liquid: solid ratio of 10% (w/w) at 121 °C for 15 min. Black liquor was separated by filtration followed by washing to neutral pH. The filtrate was dried and coded as alkali-treated (al). The alkali-treated solid part was then modified by acid treatment (ac) and acetylation (ace) (53). Acid-treated samples were obtained after subjecting the alkali-treated solid part to H_2SO_4 (5%, w/w) at a liquid: solid ratio of 5% (w/w) at 50°C for 3 h. After mild hydrolysis, the filtrate was washed several times and dried for 24 h at 80 °C. The acetylation reaction was performed by soaking the alkali-treated solid part in glacial acetic acid. The reaction was carried out by adding ethanol and concentrated H_2SO_4 (acid catalyst) at 50 °C for

3 h. After washing with water several times, the filtrate was obtained and dried for 24 h at 80 °C. The al-, ac-, and ace-treated KFP-based fillers were stored at 4 °C until use. The obtained cellulose-rich structures from kiwi peels are shown in Figure 2.


Dried kiwi peels
Dried and grinded kiwi peels untreated
Alkali treated
Acid treated
Acetylated

Figure 2: Pictures of extracted structures.

Lignin and cellulose contents of dried KFPs (unt) and extracted cellulose-rich structures were determined according to Sogut and Cakmak's methods (54). The Fourier transform infrared (FTIR) spectra, ranging from 500 cm^{-1} to 4000 cm^{-1}, for KFPs (unt) and extracted cellulose-rich structures were obtained by Spectrum Two FTIR spectrometer (Perkin Elmer, USA) with an attenuated total reflectance (ATR) module.

Preparation of PLA films

PLA at 6% (w/w) was dissolved in chloroform and poured on Teflon-coated Petri dishes. Reinforced film samples were obtained by mixing KFP-based fillers at 5% (w/w) with PLA film-forming solution. Homogeneous film-forming solutions were cast and dried at room temperature. The pouring amount of film-forming solution was adjusted to control the film thickness. All film samples were conditioned at 25 °C and 53% relative humidity (RH) for one week before characterization analyses. PLA film, which did not include any filler, was named control film. Other film samples were called PLA-unt, PLA-al, PLA-ac, and PLA-ace for PLA films, including unt, al, ac, and ace, respectively (Figure 3). The thickness of six randomly selected points was measured by a digital micrometer (Quantu-Mike IP65, Mitutoyo, Japan, ±0.001 mm).

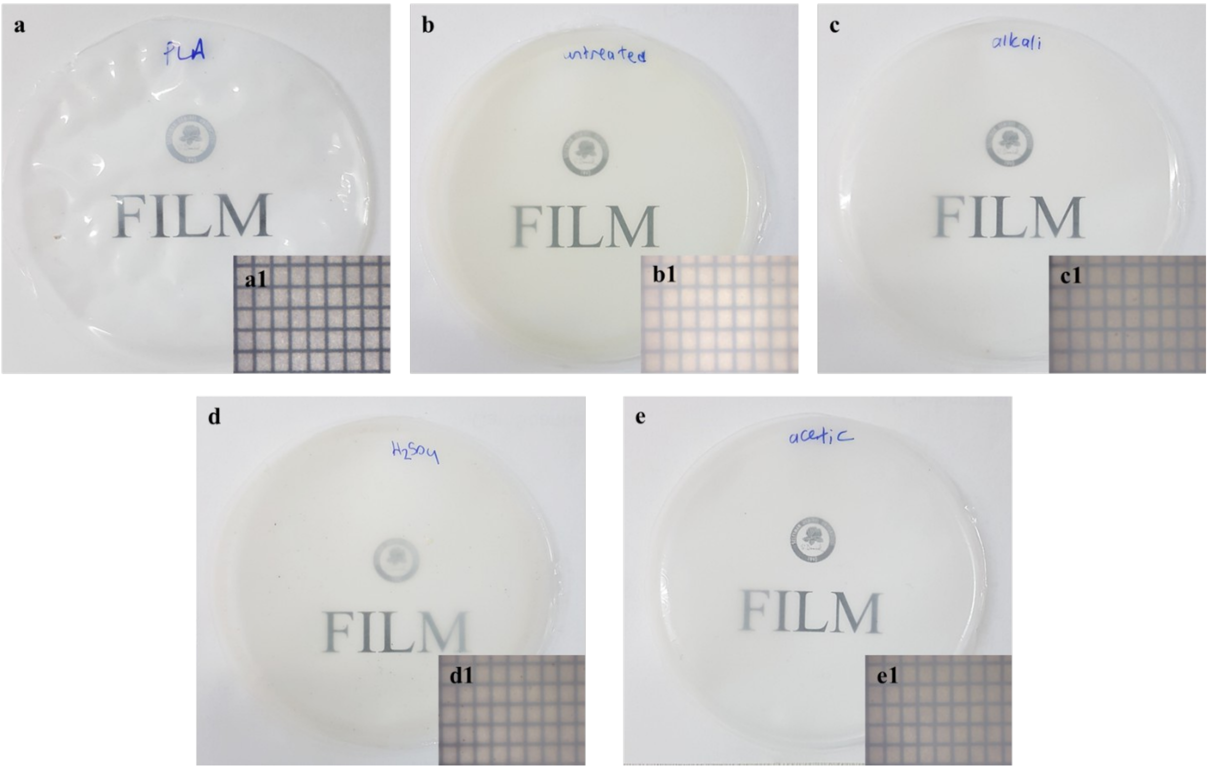

Figure 3: Pictures of film samples (a=PLA, b=PLA-unt, c=PLA-al, d=PLA-ac, e=PLA-ace and number 1 denotes images taken under a stereomicroscope (Carl Zeiss Stemi 5800, Oberkochen Germany) processed with Zeiss Zen (blue edition) software and with the scale of 0.1 mm)

Characterization of the Film Samples

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of film samples were recorded using Spectrum Two FTIR spectrometer (Perkin Elmer, USA) equipped with a horizontal ATR module, which was recorded from 500 cm^{-1} to 4000 cm^{-1} at 25 °C (with a resolution of 4 cm^{-1}).

Mechanical properties and water vapor permeability (WVP) of film samples

The mechanical properties, tensile strength (TS), and elongation-at-break values (E) were determined by the ASTM standard method D882 (55). Films were mounted in the film-extension grips of the universal testing machine (Lloyd LR5, AMETEK, Inc, UK) and stretched at 50 $mm.min^{-1}$.

The WVP of films was determined according to the E96/E96M-16 gravimetric method (56). Film samples were exposed to 100% RH, and the permeability measurements were performed by weighing the cups periodically (every 1.5 h for 48 h) at 25°C.

Optical properties of film samples

The opacity of film samples was determined using the absorption spectrum of the film sample (1×4 cm rectangular film strips) between 400 nm and 800 nm by a UV-visible spectrophotometer (Shimadzu, UV-1601, Japan). The opacity was expressed as absorbance units per film thickness (AU $nm.min^{-1}$). The transmittance values were obtained at 450 nm as percent transmittance with a UV-visible spectrophotometer (Shimadzu, UV-1601, Japan).

The color of the prepared films was determined by a Minolta Chroma Meter (CR-400, Konica Minolta, Inc., Japan). CIE L* (lightness), a* (red-green) and b* (yellow-blue) coordinates in the color space were recorded by using a white standard calibration plate (Y=92.7, x=0.3160, y=0.3321) as the background for color measurement of the films.

Statistical Analysis

An analysis of variance (ANOVA) and Tukey's multiple comparison tests were used to find the differences between film samples at a 95% confidence level. The statistical analysis was performed using Minitab 17 software (Minitab Inc., Brandon, UK). Three observations were performed for each sample, and each experiment was replicated three times.

RESULTS AND DISCUSSION

Properties of kiwi fruit peels

The cellulose and lignin contents of untreated and treated kiwi peels are shown in Table 1.

Table 1: Lignin and cellulose contents of extracted structures.

Sample	Cellulose (%)	Lignin (%)
Untreated	13.66 ± 2.22^{c}	29.93 ± 7.74^{a}
Alkali treated	37.03 ± 2.66^{b}	19.28 ± 1.46^{a}
Acid treated	65.28 ± 4.49^{a}	16.35 ± 1.77^{a}
Acetylated	35.93 ± 6.27^{b}	19.90 ± 5.38^{a}

$^{a-c}$ Different superscripts in the same column are significantly different ($p<0.05$).

It was observed that untreated KFP consisted of 13.66±2.22 and 29.93±7.74% cellulose and lignin, respectively. After the alkali treatment, cellulose content increased while lignin content decreased, showing the partial removal of lignin constituents. The same trend was also observed in acid treatment and acetylation, which might be due to the functionalization of lignocellulosic structures by reacting with cellulosic -OH groups. The acetylation process might also modify the fiber structure, causing an increase in plasticization and a reduction in the water affinity of cellulose (57). Similarly, Narender and Priya Dasan (58) and Kocaman and Ahmetli (53) observed a reduction in lignin concentration after acid treatment and acetylation of coir pith and hazelnut shells, respectively.

The FTIR spectra of KFP and treated KFPs are shown in Figure 4.

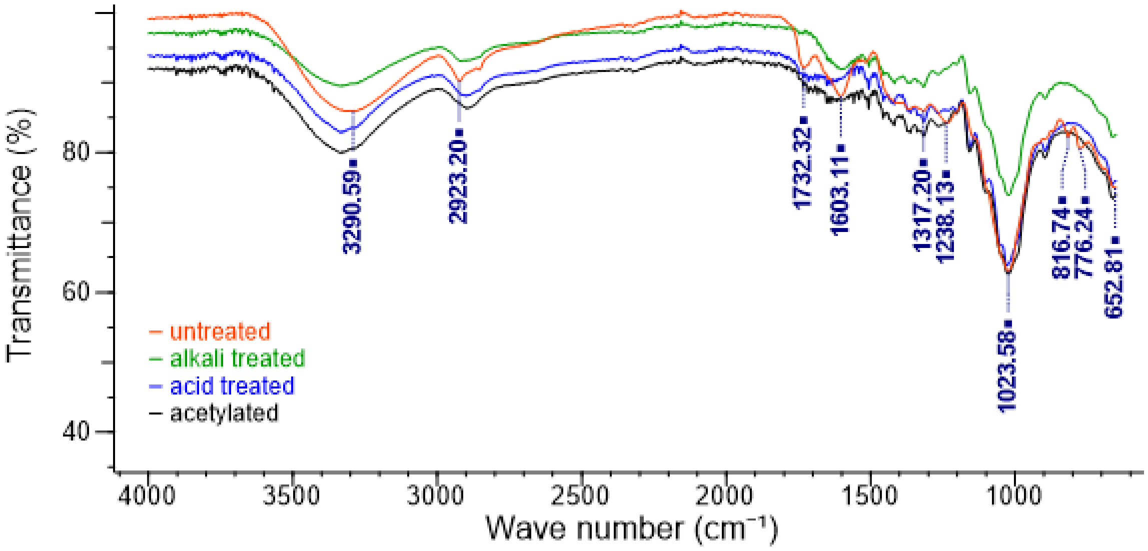

Figure 4: FTIR spectra of untreated, alkali-treated, acid-treated, and acetylated kiwi peels.

The peaks found at 3300 cm^{-1}, 1600 cm^{-1}, and 1700 cm^{-1} belong to the O–H stretching, the aromatic C=C stretching, and the unconjugated C=O groups stretching. The peaks found at 1220 cm^{-1} are also assigned to the C-O stretching in lignin rings. The peak at 900-1100 cm^{-1} belongs to the cellulosic linkages, and the changes in the intensity of these peaks are associated with the changes in cellulose levels after the treatments. The disappearance of peaks around 1700-1800 cm^{-1} observed after the chemical treatments can be related to the decline in or the removal of hemicellulose-based structures. Besides, the intensity of peaks at 1220 cm^{-1} was lower than the untreated KFP structures, which can be correlated with the reduction in lignin concentration due to the chemical treatments. The band at 1245 cm^{-1} might be observed due to the presence of the acetate groups. Similar behavior was observed by Sreekala et al. (59) for oil palm fiber and Kocaman (60) for apricot kernel shells after various chemical modifications.

Properties of film samples

The thickness, water vapor permeability (WVP), and mechanical properties of film samples are shown in Table 2.

Table 2: Thickness, water vapor permeability (WVP), and mechanical properties (TS, E) of film samples.

Sample	Thickness (µm)	WVP (g.mm.kPa^{-1}.h^{-1}.m^{-2})	TS (MPa)	E (%)
PLA	113±15^{a}	0.15±0.05^{a}	19.55±1.88^{a}	4.32±0.19^{a}
PLA-unt	150±20^{a}	0.12±0.01^{b}	21.44±1.66^{a}	3.98±0.53^{a}
PLA-al	128±35^{a}	0.11±0.03^{b}	27.55±7.81^{a}	4.79±0.61^{a}
PLA-ac	150±21^{a}	0.11±0.02^{b}	29.67±5.25^{a}	4.92±0.62^{a}
PLA-ace	128±38^{a}	0.10±0.01^{b}	26.14±4.38^{a}	4.70±0.25^{a}

$^{a-b}$ Different superscripts in the same column are significantly different ($p<0.05$).

The thickness of film samples slightly increased with the addition of fillers; however, the fillers did not significantly affect the thickness of film samples. The highest thickness values were observed in PLA-unt and PLA-ac film samples due to less compatibility and lower interaction between the CH film matrix and the filler.

The addition of KPF-based fillers into PLA films significantly lowered the WVP of film samples, and the lowest values were found in PLA-ace film sample ($p<0.05$). The dispersion of fiber particles within the film matrix might affect the diffusion way of water molecules by changing the polarity of polymer and the path length of water molecules (61). Similar results were observed by Khalil et al. (62), who studied the effect of bamboo fibers on the thermo-mechanical properties of carrageenan films, and Valdés García et al. (63) used almond skin residues to improve the properties of PCL films.

The application of different chemical treatments had various effects on the mechanical properties of film samples. Compared to neat PLA films, TS and E values increased after alkali treatment and modifications made by acetylation and acid treatment. The PLA films, including untreated KFP, also showed an increase in TS while a reduction was observed in elongation. The differences between untreated fiber added PLA film and PLA films, including alkali-treated and modified KFP, might be due to increased cellulose content and improved adhesive characteristics obtained after chemical treatments (64). Acid-treated kiwi peels had the highest cellulose concentration, followed by alkali-treated and acetylated samples, while untreated peels had the lowest cellulose concentration. The presence of high cellulose fiber content might favor the interfacial adhesion between PLA and filler, resulting in better interactions with higher tensile strength. The addition of untreated peels had lower TS values, showing the modification improved the filler-matrix adhesion at the interface through the reaction with end groups of PLA (65). The direct use of lignocellulosic structures in polymeric matrices results in poor compatibility, requiring modifications to obtain a larger surface area for better interactions between filler and polymer (66). The chemical modifications used in the experiments might substitute the hydroxyl groups of peels with other functional groups depending on the used method, making the fiber more hydrophobic and thus enhancing the TS of polymer (21).

Similarly, Kocaman et al. (64) also reported enhanced mechanical properties for biobased composite materials when chemically modified coconut waste particles were incorporated. The elongation at break is related to the flexibility of polymer chains; thus, an inverse effect is expected between TS and elongation. However, in this study, both TS and E values increased with fillers. The presence of lignin could also contribute to the plasticization of PLA due to the lignin-PLA bonding at the interphase regions (26).

The optical properties of film samples are shown in Table 3.

Table 3: Optical properties of film samples.

Sample	*L**	*a**	*b**	Transmittance (%)	Opacity (AU nm/µm)
PLA	96.33 ± 0.27^a	0.14 ± 0.03^a	1.82 ± 0.11^c	47.85 ± 6.70^a	4.42 ± 0.32^a
PLA-unt	91.72 ± 1.30^b	0.63 ± 1.23^a	11.19 ± 2.15^a	27.58 ± 2.01^{ab}	4.99 ± 0.30^a
PLA-al	91.42 ± 1.93^b	1.28 ± 0.60^a	6.11 ± 1.37^b	27.80 ± 7.33^{ab}	4.23 ± 0.18^a
PLA-ac	92.05 ± 1.80^b	1.40 ± 0.76^a	7.86 ± 1.74^b	24.40 ± 4.34^b	4.26 ± 0.41^a
PLA-ace	93.49 ± 0.49^{ab}	0.66 ± 0.29^a	4.80 ± 0.60^{bc}	29.10 ± 1.67^{ab}	4.97 ± 0.89^a

$^{a-c}$ Different superscripts in the same column are significantly different ($p<0.05$).

PLA control film had the high *L** value indicating its brightness and transparency, while its *a∗* and *b∗* values were close to zero. The lightness of films, including untreated and alkali-treated KFPs was the lowest, followed by acid-treated and acetylated KFP added PLA films ($p<0.05$). The *a** and *b** values significantly increased with the addition of fillers as indicative of a red, yellowish/brown coloration, which is due to the typical color of KFPs. This behavior was also reflected as a significant decrease in transmittance and a significant increase in opacity. The lowest value was measured for the PLA-ac film, which might be due to the weak dispersion of the acid-treated lignin within the PLA matrix. The low transmittance values demonstrated the potential applicability of these films as UV-blocking films mainly for light-sensitive products (67). Similar behavior was observed by Wang et al. (68) for PLA and grafted PLA films, including lignin.

The FTIR spectra of film samples are shown in Figure 5.

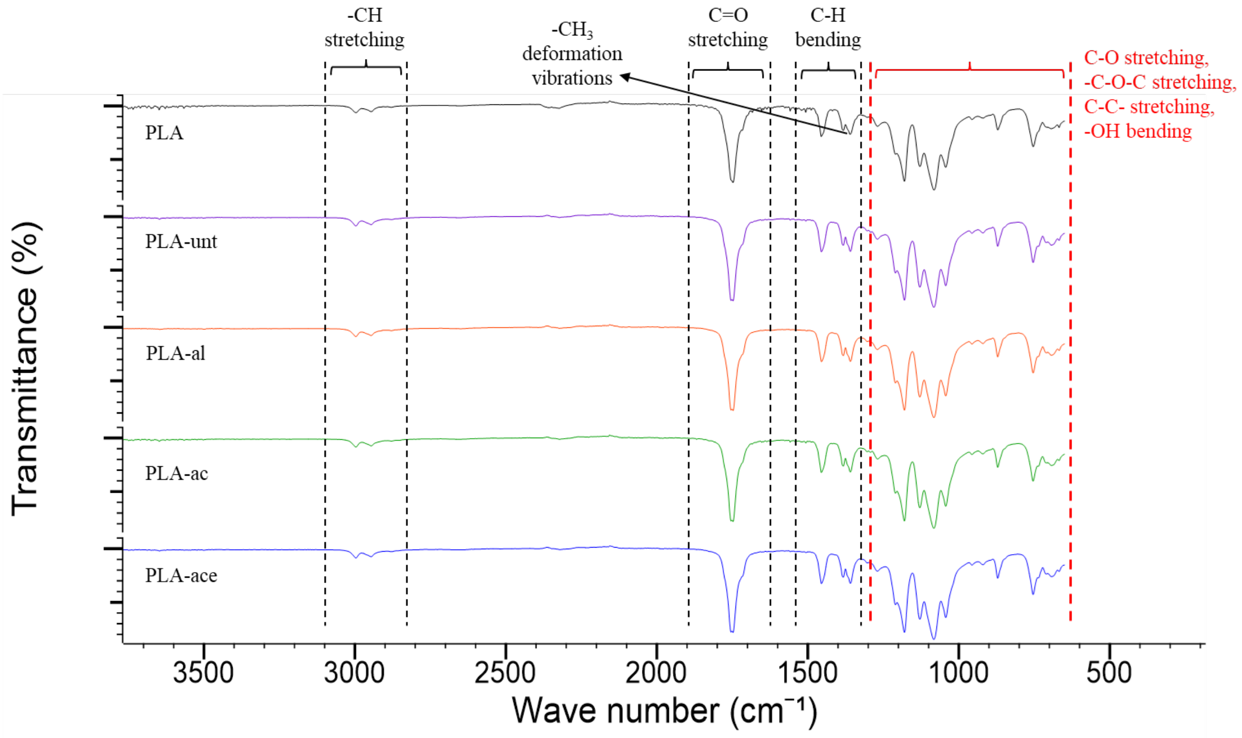

Figure 5: FTIR spectra of film samples.

The major peaks of PLA showed in Figure 5 are at 1750 cm^{-1} assigned to the –C=O stretching vibration of the ester group, and the peaks between 1300-1400 cm^{-1} corresponded to the asymmetric and symmetric -CH$_3$ deformation vibrations, respectively. The other peaks identified between 800 and 1300 cm^{-1} are related to the –C-O-C-stretching of the ester groups, the C-O stretching, the -OH bending, and the –C-C- stretching of the amorphous phase (69). Iglesias Montes et al. (70) observed similar FTIR spectrums for PLA bilayer films containing cellulose nanocrystals or lignin nanoparticles. The structure of PLA films did not vary with the addition of KFP-based fillers, as confirmed by any differences in FTIR spectra compared to those of neat PLA films. Opposite to these results, Nair et al. (26) found considerable interactions between the nanocellulose fibrils with high lignin content and PLA film matrix, which might be due to the differences in lignin particle size having an impact on particle-matrix interface adhesion.

CONCLUSION

Lignocellulosic structures were extracted from KFPs by alkali treatment and alkali combined chemical treatments such as acetylation and acid treatment. It was observed that the lignin concentration decreased while the cellulose concentration increased after alkali treatment and chemical modifications of lignocellulosic structures extracted from KFPs. The obtained structures were then added to the PLA film-forming solutions to enhance the PLA film properties as a food packaging material. The WVP, TS, and elongation of PLA films were enhanced with alkali-treated and alkali combined chemically modified structures. However, no significant changes in the chemical structure of PLA upon the addition of various KFP-based fibers as confirmed by FTIR spectra. In conclusion, alkali treatment and different modifications were found to have the potential to modify the lignocellulosic structures extracted from agricultural wastes to be used as fillers in the polymeric matrix for the improvement of film properties.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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