



Effect of palm wax on the mechanical, thermal, and moisture absorption properties of thermoplastic cassava starch composites

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ABSTRACT

Thermoplastic starch is a potentially sustainable and biodegradable material. However, it possesses some limitations in terms of mechanical performance and high moisture sensitivity. In this current work, the characteristics of thermoplastic cassava starch (TPCS) containing palm wax at various loading were evaluated. TPCS was prepared via hot pressing by varying the ratios of palm wax (2.5, 5, 10, and 15 wt%). Next, characterization via scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FT-IR), mechanical, water solubility, thickness swelling and moisture absorption tests, were conducted on the samples. The findings showed that incorporating starch-based thermoplastics with palm wax has remarkably improved mechanical characteristics of the thermoplastic blends. Besides, the morphology of the samples demonstrated irregular and rougher cleavage fracture after palm wax addition. FT-IR indicated the existence of intermolecular interaction between TPCS and palm wax with the intermolecular hydrogen bonds that existed between them. The thermal stability of TPCS has improved with rising palm wax content. The incorporation of 15 wt% palm wax resulted in the lowest moisture absorption value among the samples. Overall, the developed TPCS/palm wax with improved mechanical and moisture resistance characteristics has the potential to be used as biodegradable materials.

1. Introduction

Environmental challenges and global ecology have directed crucial attention to biodegradable materials derived from renewable sources. The majority of synthetic plastics are unable to degrade naturally, causing serious environmental problems of pollutions. Incineration of non-biodegradable polymer wastes has serious drawbacks, including high cost and harmful gases emission to the environment. Therefore, it is urged that new, effective, environmentally friendly, and biodegradable materials are required for advanced applications. Fabrication of bio-derived polymers with the aim to substitute petroleum-based products is essential to alleviate the pressures of resource scarcity. Bio-based polymers are among the most practical solutions for reducing current environmental issues. Numerous bio-based polymers have been produced due to their renewable nature and widespread availability at a

low cost.

Starch is among the most promising biopolymers and has been considered to suit many industrial needs owing to its renewability, abundant availability, biodegradability, and competitive price [1–3]. It is derived from numerous natural resources, e.g., corn, potato, sago, and cassava. In general, starch comprises completely biodegradable polysaccharides containing linear α -1 amylose, 4 bonded glucose units, and short α -1 highly branched amylopectin, 4 glucan linked by α -1, 6 linkages at the branch points [4,5]. Besides its great advantages, starch also possesses drawbacks due to its hygroscopic behaviour, as well as poor mechanical and thermal characteristics [6,7]. Starch is semi-crystalline granules and must be plasticized in order to enhance the final products' flexibility and properties [8]. Numerous plasticizers are being utilized for starch plasticization, e.g., glycerol, citric acid, sorbitol, and additives [9,10]. Plasticizers have been extensively reported to improve starch's

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thermal stability, tensile strength, and water resistance [7,11].

Cassava (also known as *Manihot Esculenta*) is a traditional subsistence crop in tropical areas and possibly native to the Amazon region. According to reports, cassava starch comprises 17–20% amylose that has a greater molecular weight than other starch-based amyloses [12]. Besides that, cassava is a high-energy food that contains over 80% starch and is high in vitamin C, minerals, and carotenoids [13]. Despite its great advantages like abundant supply, cheap, and biodegrades easily, starch from cassava is extensively used to develop biodegradable packaging films [14], rigid containers [15], edible food coatings [16], and other applications around the globe. The starch potential as a renewable and biodegradable thermoplastic source has prompted researches into the forthcoming of cassava starch as feedstock for biodegradable thermoplastic, even though thermoplastic starch experiences a significant limitation of being hydrophilic.

Thermoplastic starch has gained considerable attention recently due to its thermoplastic-like processability using plasticizers under high temperatures and shear [17]. During the process, the plasticizer is introduced to native starch and thoroughly blended before the plasticization takes place. Thus, the new hydrogen bonds generation between starch and plasticizer were simultaneous with the breaking down of the starch molecules' hydrogen bonds [18]. Despite the promising alternatives for developing environmentally friendly characteristics of thermoplastic starch, it has some drawbacks that limit the application. Nevertheless, thermoplastic starch has two major drawbacks: poor mechanical strength and high water absorption [19]. Blending thermoplastic starch with other comparatively hydrophobic materials is one of the most efficient approaches to overcome those limitations due to its simplicity, rapidity, and low cost [20]. Incorporating synthetic polymers with thermoplastic starch will compromise the biodegradability of the materials. As a result, using natural-based material as an element of the thermoplastic starch blend is more desirable and practical. A previous study showed that thermoplastic starch blended with synthetic polymers, for instance, poly (lactic acid) (PLA), increased the mechanical performance of thermoplastic starch and the biodegradation rate of the blends [13]. Moreover, the potentials of numerous materials as components for thermoplastic starch were also studied, i.e. wax, chitin, chitosan, and carrageenan [12,21–23].

Palm wax originates from palm oil and is derived from the *Elaeis guineensis* fruit during a few stages of the refining process. It comprises long-chain saturated fatty acids, e.g., palmitic acid ($C_{16:0}$) and oleic acid ($C_{18:1}$) that contribute to its great hydrophobic character. Palm wax has a melting temperature of approximately (58–60 °C), which is lower than beeswax (62–66 °C), carnauba wax (82–86 °C), and Candelilla wax (68.5–72.5 °C). Thus, it is well-suited for use in conjunction with thermosensitive active compounds such as phenols or terpenoids, which require low processing temperatures. Furthermore, because saturated molecules form a huge percentage of their chemical components, they are less vulnerable to autooxidation, which predominantly attacks the double bonds. As a result, it has the ability to retain oxidative stability for an extended duration. Palm wax is seen as a cost-effective alternative to fossil-based hydrophobic chemicals that also meet environmental criteria.

Recently, the effect of wax on natural polymers, such as chitosan biofilm [24], pullulan [25], and gelatin [26] has been investigated. It was noted that there are interactions between starch matrix and wax indicated through FTIR analysis due to the hydrogen bonding network formed between them. This enhanced the biopolymer's performance such as water barrier properties and mechanical strength as well as enhancing their uniqueness as edible food coatings and food packaging materials [25,27,28].

Even though there are studies reported on using thermoplastic cassava starch (TPCS) as the matrix in composites, none has reported the utilization of palm wax in the TPCS matrix. Hence, this study is aiming to study the palm wax effect on the thermal, mechanical, thickness swelling, water solubility and moisture absorption behaviour of the

materials.

2. Materials and methodology

2.1. Materials

Cassava starch of food grade was purchased by Antik Sempurna Sdn. Bhd, (Selangor, Malaysia) and palm wax (PW) (palmitic acid, $C_{16:0}$ = 59.09% and oleic acid, $C_{18:1}$ = 39.55%) was purchased from Green & Natural Industries Sdn. Bhd, (Selangor, Malaysia). Analytical grade glycerol (99.5% purity) as plasticizer was obtained from QRec Chemicals Sdn. Bhd., (Selangor, Malaysia).

2.2. Sample preparation

Preparation of thermoplastic cassava starch (TPCS) samples was conducted by adding 30 wt% glycerol prior to pre-mixing in a Panasonic MX-GM1011 Dry Mixer at 1200 rpm for 5 min at ambient temperature. The resulting blend was then thermo-pressed at 150 °C for 60 min using a GOTECH Testing Inc. GT7014-P30 C Plastic Hydraulic Moulding Press (Taichung City, Taiwan) under 10 t load to produced sheets having 3 mm thickness. A similar procedure was also used for the TPCS preparation with palm wax. The matrix's properties modification was conducted by employing various palm wax ratios (2.5, 5, 10, and 15 wt%). The prepared samples were immediately stored in a silica gel-filled desiccator before the conditioning phase to prevent unwanted moisture absorption.

2.3. FT-IR analysis

Fourier transform infrared (FT-IR) spectroscopy was chosen and used to identify functional groups that exist between thermoplastic starch and palm wax. The spectrum of each material was attained using JASCO FTIR-6100 Spectrometer (Japan). The samples' FT-IR spectra were studied in the 4000–500 cm^{-1} range.

2.4. Scanning electron microscope (SEM)

The morphological characteristics of tensile fractured samples were studied by a scanning electron microscope (SEM), Zeiss Evo 18 Research, (Jena, Germany) at 10 kV acceleration voltage. The samples were cut to similar sizes and their surfaces were gold-coated before the test. The tensile test specimens that underwent testing were kept in zip-locked containers and characterized via SEM.

2.5. Thermogravimetric analysis (TGA)

The analysis of the composites' thermal degradation was performed in TGA indicated by the loss of weight as a function of temperature increase. TGA was carried out with a Q series thermal analysis machine, Mettler-Toledo AG, Analytical (Switzerland) to study the samples' thermal stability in aluminum pans, temperature (25 to 600 °C), constant heating rate (10 °C/ min^{-1}), and dynamic nitrogen atmosphere. The differential of TGA values resulted in the derivative form of TGA (DTG).

2.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis was carried out on 5 mg of prepared samples, which were weighed and then put in an aluminum sample pan and was instantly sealed, where the point of reference was determined using an empty sample pan. All samples were heated at a 10 °C/min heating rate using DSC equipment (UniversalV3-9ATA Instrument, New Castle, PA, USA). The inert environment was maintained by flushing nitrogen gas in the DSC cell at a 20 mL/min flow rate. The thermogram results were used to determine the transition

temperatures.

2.7. Tensile testing

Tensile tests were performed following ASTM D638 at a relative humidity of $50 \pm 5\%$ and temperature of $23 \pm 1^\circ\text{C}$. Five (5) replications of the tests were conducted in a Universal Testing Machine (INSTRON 5969), INSTRON (United States) at 5 mm/min crosshead speed equipped with a 50 kN load cell. The tensile properties results were determined by calculating the data mean.

2.8. Flexural testing

A flexural test was conducted at a temperature of relative humidity of $50 \pm 5\%$ and $23 \pm 1^\circ\text{C}$ in accordance with ASTM D790. The samples having 130 mm (L) \times 13 mm (W) \times 3 mm (T) dimensions were prepared. Five (5) replications were used during the testing using Universal Testing Machine (INSTRON 5969), INSTRON (United States) at 2 mm/min crosshead speed and 50 kN load cell.

2.9. Impact testing

ASTM D256 was employed during the Izod impact tests conducted at $23 \pm 1^\circ\text{C}$ temperature and $50 \pm 5\%$ relative humidity. The samples with 60 mm (L) \times 13 mm (W) \times 3 mm (T) dimensions were prepared and five (5) replications of each sample were used in a digital pendulum impact tester, Victor Equipment Resources Sdn. Bhd. (Malaysia). The specimens' cross-section area and impact energy were considered in the determination of the impact strength (Eq. (1)). Preconditioning of all samples took place for 2 days before processing for 2 days at 53% RH prior to testing at 53% RH.

$$\text{Impact strength} = \text{Impact energy (J)} / \text{area (mm}^2\text{)} \quad (1)$$

2.10. Moisture absorption

For the moisture absorption investigation, TPCS/palm wax samples were placed at $25 \pm 2^\circ\text{C}$ temperature and $75 \pm 2\%$ relative humidity (RH) in a shut humidity chamber to analyze the samples' moisture absorption behaviour. Five (5) samples having 10 \times 10 \times 3 mm dimensions were prepared and dried for 24 h at $105^\circ\text{C} \pm 2$ prior to the moisture absorption measurements. The specimens were weighed prior and after absorption, indicated by W_i and W_f , respectively (Eq. (2)) for a specific duration until the stable weight was achieved. The samples' moisture absorption was computed via Eq. (2):

$$\text{Moisture Absorption (\%)} = \frac{W_f - W_i}{W_i} \times 100 \quad (2)$$

2.11. Water solubility

Water solubility of the samples was conducted by using the method developed by Zhang et al. [29] with slight modifications. Five (10 mm \times 10 mm \times 3 mm) samples were cut, dried in an oven for 24 h at $105^\circ\text{C} \pm 2$, and each sample's initial dry matter recorded as W_i . Afterwards, immersion of each sample in 30 ml distilled water and constant agitation. Then, after 24 h immersion, the undissolved fractions of sample were collected from the beaker and residual water on the sample's surface was removed using a filter paper. Lastly, the samples were re-dried at $105^\circ\text{C} \pm 2$ temperatures for 24 h to determine the final dried sample, recorded as W_f . The determination of the samples' water solubility was computed as follows.

$$\text{Water Solubility (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (3)$$

2.12. Thickness swelling

The samples' swelling analysis was performed following the improved procedure by Jawaid et al. [30]. Five (10 mm \times 10 mm \times 3 mm) samples were cut and oven dried for 24 h at $105^\circ\text{C} \pm 2$. Before testing, the thickness of each sample were recorded. Afterwards, each sample was immersed in 30 ml distilled water at for 2 h ambient temperature ($23 \pm 1^\circ\text{C}$). A digital vernier calliper (Model: Mitutoyo) with a 0.01 cm precision was used to measure the initial and final thicknesses, T_i , and T_f , during the immersion process. The samples' thickness swelling ratio was computed as follows:

$$\text{Thickness swelling (\%)} = \frac{T_f - T_i}{T_i} \times 100 \quad (4)$$

2.13. Statistical analysis

One-way analysis of variance (ANOVA) was used to determine the significance of each mean property value ($p < 0.05$), and Duncan's multiple range test was used to assess the significance of each mean property value ($p < 0.05$).

3. Results and discussions

3.1. FT-IR analysis

Fig. 1 displays the FT-IR spectra for cassava starch and palm wax, while Fig. 2 presents the FT-IR of TPCS with varying palm wax concentrations. A wide wavelength range at 3200–3500 cm^{-1} corresponded to the hydroxyl groups (-OH) stretching vibrations associated with the complex vibrational stretching related to free, inter-, and intramolecularly bounded hydroxyl groups [31]. The band at about 2923 cm^{-1} could be ascribed to C–H stretching from CH_2 and/or CH_3 conjugated bending vibrations that existed in all blended samples [24]. The IR spectrum supplemented with palm wax also demonstrated other absorption regions linked to the wax's functional groups. Next, the existence of fatty acid chains in palm wax created sharp peaks at 2848 cm^{-1} that revealed the methylene symmetric and asymmetric stretching vibrations from aliphatic C–H groups existed in the majority of hydrophobic components and lipids. They were much more noticeable and grew in intensity with higher wax concentration [32]. These outcomes were also confirmed by Muscat et al. [33] in their work on the spatial distribution of wax. The intensified CH_2 stretching vibrations at 2849 cm^{-1} in the study were a result of the concentration and distribution of wax. Aside from the peak upshift, the peak at 1655 cm^{-1} might indicate

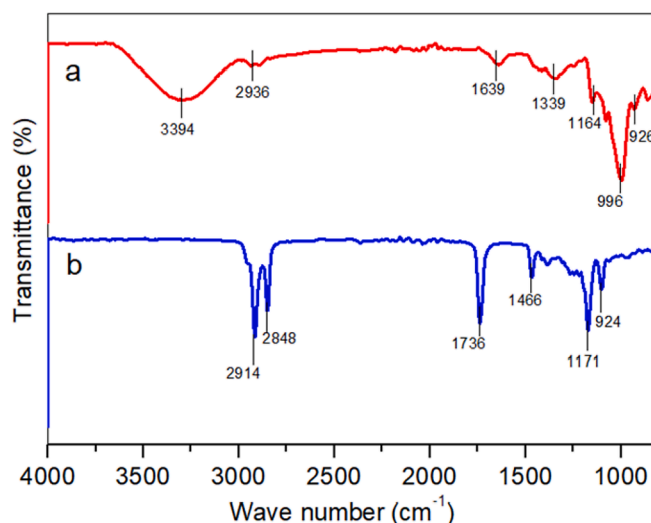


Fig. 1. FT-IR spectra of (a) native cassava starch and (b) native palm wax.

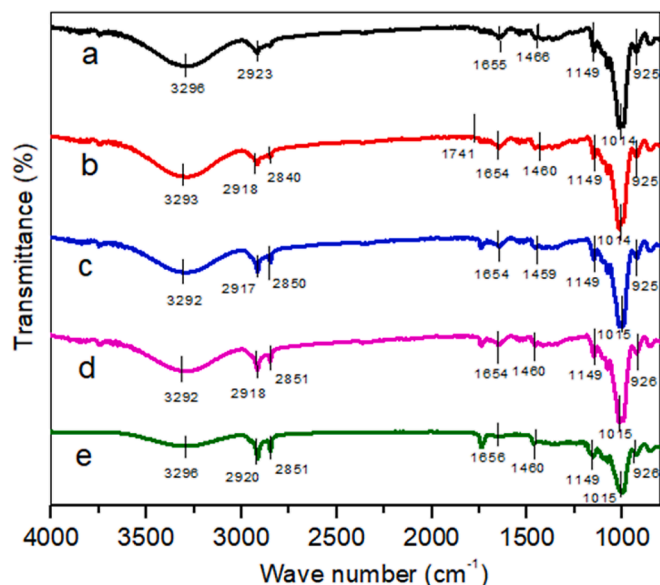


Fig. 2. FT-IR spectra of (a) neat cassava starch matrix (b) 2.5% palm wax (c) 5% palm wax (d) 10% palm wax (e) 15% palm wax.

the C=O (carbonyl) stretching; meanwhile, additional peaks in the range 1400–1450 cm^{-1} were assigned for the hydroxyl (-OH) groups [34]. In the TPCS spectrum range, three peaks occurred in the 928 and 1164 cm^{-1} range ascribed with C—O bond stretching [35].

Chemical or physical interactions between different compounds in a mixture are shown by the spectra peak changes. Small differences in intensity and band displacement can be associated with the interaction between the starch functional groups and palm wax. The band intensities increase between 2918 and 2840 cm^{-1} associated to the CH_2 elongation for samples incorporated with palm wax. This can be ascribed to the huge number of alkanes and long-chain fatty alcohols, a common characteristic of these waxes [36]. Another absorption band appeared at 1741 cm^{-1} was related to C=O stretching vibrations of the functional group ester carbonyl was found when palm wax was added. This peak intensity was noticeable increased with increasing of palm wax content [29]. The absorption peak at 1540.47 cm^{-1} corresponded to the C—N stretching and N—H bending vibrations remain unchanged in the all samples.

In addition, the chemical interaction between material components can be indicated through the shifting of broadband at 3100–3700 cm^{-1} (O—H stretching) to smaller wavenumber value [35]. The polymer blends exhibited the O—H group peak shift from 3296 towards 3292 cm^{-1} after the palm wax addition, indicating the existence of new hydrogen bonding formations between the starch and palm wax [37]. Similar starch-wax interaction has been reported previously on the development of arrowroot starch-carnauba wax films [36]. The peak shift in this range also denoted potential compatibility between these two constituents and showed the interaction of filler and matrix. This interaction is consistent with the mechanical properties improvement of the material following the addition of palm wax, which enhanced the strength of the materials.

3.2. Scanning electron microscope (SEM)

The images from SEM of the fractured TPCS/palm wax composites surfaces are presented in Fig. 3. The TPCS revealed a compact structure devoid of porosity as well as the undissolved starch particles presence. The control surface (Fig. 3a) contains a homogenous surface with no apparent phase separation, suggesting good interaction between starch and glycerol [38]. However, after the palm wax incorporation into TPCS, it was observed that the samples' surfaces exhibited less

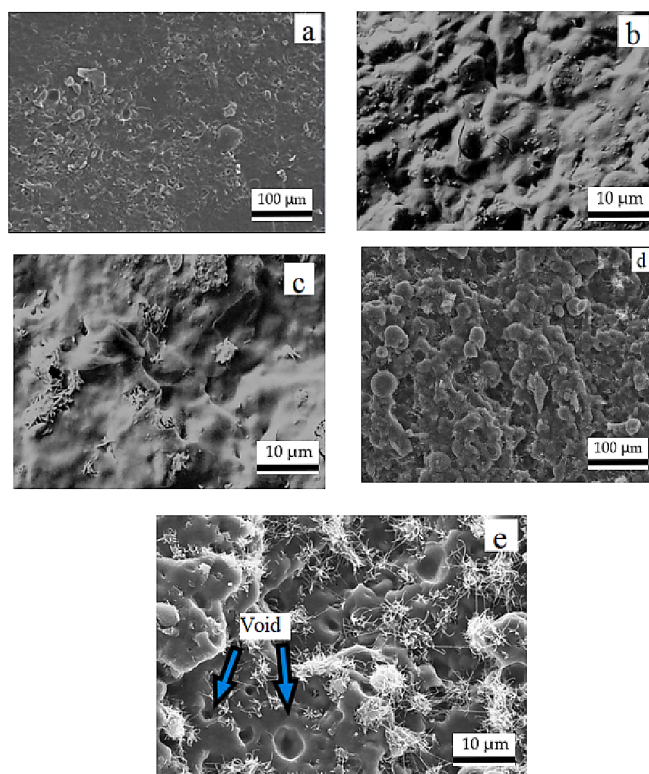


Fig. 3. SEM micrograph of fracture surface of TPCS blended with different ratios of palm wax (a) 0 wt% (b) 2.5 wt% (c) 5 wt% (d) 10 wt% (e) 15 wt%.

homogeneity, resulting in a non-uniform and rigid structure with an irregular surface as demonstrated in Fig. 3b–e. Besides, it was found that as the filler content was raised from 0 to 15 wt%, the fracture surface showed irregularity and the presence of pores. This might be attributed to starch retrogradation, where palm wax interfered with starch plasticization and thus resulted in the phase separation appearance between TPCS and palm wax, particularly at higher palm wax content (15 wt%), as shown in Fig. 3e. Furthermore, the existence of voids found at 15 wt% filler indicated the interaction between starch/palm wax that was relatively low ascribed to the addition of high filler amount and the inability of proper hydrophilic starch mixing with hydrophobic wax matrix [36]. This was due to discontinuity in the matrix and it started to agglomerate at higher filler content [36]. These findings were parallel with the outcomes from pea starch reinforced with carnauba wax [39]. Nevertheless, the structure was observed to be less consistent, and weak interface or stress concentration sites for crack initiation and propagation were formed, resulting in the easy failure of composites under applied tensile strength, as illustrated in (Fig. 5a, discussed later) where the higher content of wax (15 wt%) significantly reduced the tensile strength. A similar result was observed in the study on development cassava starch reinforced carnauba wax composites [40].

3.3. Thermogravimetric analysis (TGA)

The thermal degradation and stability of native palm wax, native cassava starch, and their blends were determined from the TGA and DTG curves that were plotted as the percentage sample weight loss and its derivative against temperature, as presented in Fig. 4. It is observable that there was a three-step degradation process for the samples. The first step occurred below 100 °C, which might indicate the water molecules' elimination by the evaporation [41]. The stage took place in the temperature range of 41.7–106 °C with 1.6–3.95% weight loss that was possibly linked to the free water loss. Nevertheless, the first stage of weight loss for native palm wax seem was not detected. This might be

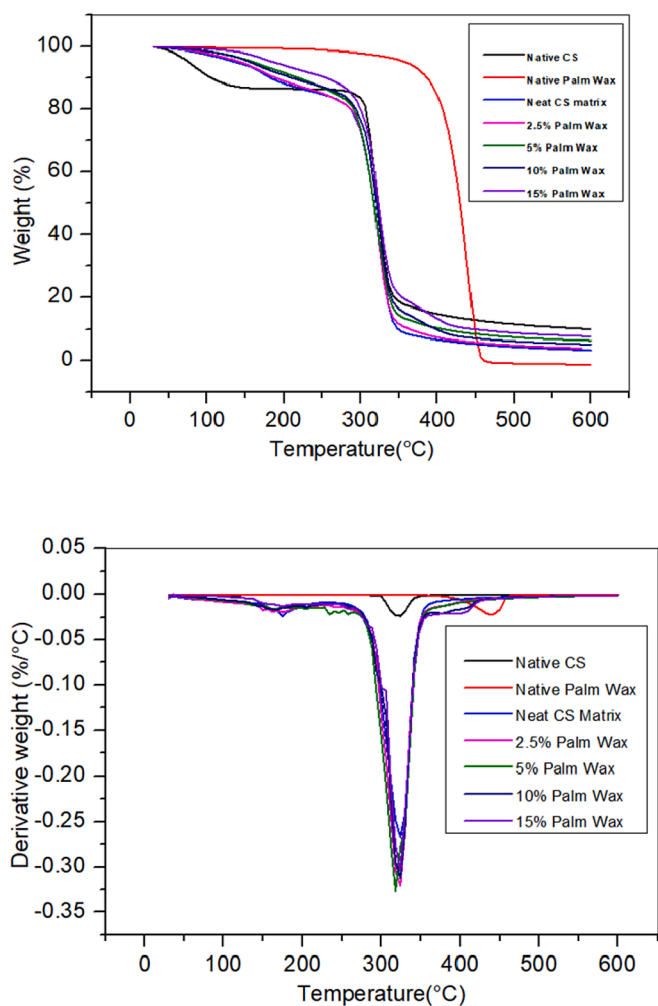


Fig. 4. TGA and DTG of TPCS blended with different ratio of palm wax.

due to the low moisture content in native palm wax as palm wax is hydrophobic with a very low capacity for retaining water. This observation was parallel to the earlier finding from the beeswax addition on the properties of gelatin films by Zhang et al. [29]. The second thermal degradation, which occurred at 125 to 290 °C temperature range, was correlated to volatile matter, bound water loss, and decomposition of plasticizers in the biopolymer [42]. A previous study reported majority of plasticizers begin to volatilize at 150 °C [43], and the glycerol's boiling point is 198 °C [44]. A similar degradation temperature of beeswax plasticizer incorporated into thermoplastic starch was also reported [45]. The second weight-loss stage of 18.9–36.4% might relate to starch, wax, and degradation of glycerol, which were mostly ascribed to hydrogen bonds provided by electrostatic and Van der Waals forces as well as steric repulsions [29]. The last thermal degradation stage was observed around 320–333 °C with 60–68% weight loss associated with cassava starch molecules' decomposition due to the breaking down of amylose and amylopectin glycosidic linkages in the starch polymer and wax [29]. The high temperature experienced by the samples at this phase was essential for the molecules of polymer to be decomposed into smaller molecules as well as their derivatives.

In addition, the thermal decomposition of native palm wax that resulted in the main loss was observed around 412–453 °C. The incorporation of palm wax (0 to 15 wt%) was found to raise the initial TPCS degradation temperature from 295 to 308 °C when the palm wax content was increased. This could be ascribed to the characteristics of native palm wax of higher initial decomposition temperature than cassava starch and the polar side groups interactions in starch (e.g., hydroxyl,

carbonyl) and wax fraction [46]. Moreover, the result showed that rising palm wax content resulted in improved thermal stability due to the increased palm wax amount that possessed better thermal stability in comparison to starch.

Meanwhile, the DTG curve was observed to gradually change in accordance with the native palm wax as the content of palm wax was increased. The DTG curves showed the maximum decomposition rate for neat TPCS, TPCS/palm wax 2.5 wt%, TPCS/palm wax 5 wt%, TPCS/palm wax 10 wt%, and TPCS/palm wax 15 wt% that were 0.26%/°C, 0.32%/°C, 0.34%/°C, 0.31%/°C and 0.30%/°C, respectively. These findings corroborated previous research by Zhang et al. [43], who discovered lower maximum degradation rate for wax-free gelatin film than for beeswax containing gelatin film. The final stage might be linked to the decomposition of the inorganic oxides produced during the thermal analysis of ash components. At the end of the degradation, the 15 wt% palm wax showed the highest amount of residue among the samples. This also indicated better thermal stability of the TPCS/palm wax than the neat TPCS. In summary, the incorporation of palm wax improved the thermal stability of the thermoplastic cassava blends. Table 1 summarises the TGA result.

3.4. Differential scanning calorimetry (DSC)

Native palm wax, cassava starch and their blends are all represented in Table 2 by their T_g and T_m values, respectively. The T_g value for native cassava starch is 162.9 °C. However, with the presence of glycerol as a plasticizer, the T_g value of TPCS was reduced to 160.3 °C. The obtained results are consistent with the findings reporting decrement in the T_g value with plasticizers incorporation into starch films made by varying amounts of plasticizer [47]. Furthermore, the decrease in T_g value might be associated to the plasticizer's role in disrupting the intermolecular interactions between polymer chains, resulting in decreased overall cohesiveness and a decrease of T_g [48]. According to the Singh et al. [49] on the development of starch-rice grain, they found that the glass transition is primarily caused by the amorphous polymer (linear, e.g., amylose), in which molecules slid over each other upon thermal energy application, resulting in the polymer becoming more flexible, viscous, and rubbery, hence led to the glass transition in starch. Meanwhile, a previous study suggested that plasticizer reduced T_g by facilitating chain mobility [50]. One of the primary challenges with starch-based materials is brittleness because of their high T_g [51]. Starch is brittle without plasticizers, hence, the inclusion of plasticizers solves the brittleness of starch and increases the polymer's flexibility and extensibility.

The incorporation of palm wax was found to raise the T_g value for thermoplastic cassava starch blends. This could be linked to the greater T_g value of native palm wax than cassava starch in this study. Furthermore, the raise in T_g was dependent on the concentration of palm wax and cassava starch, which might link to the initiation of intermolecular hydrogen bonding interactions between palm wax and cassava starch matrix. These interactions constrained the flexibility and mobility of the matrix chains, thereby, increasing the T_g value. In addition, the melting temperatures thermoplastic cassava starch blends' increased

Table 1
TGA results of TPCS/palm wax.

Samples	T_{on} (°C)	T_{max} (°C)	Weight loss at T_{max} (wt%)
Native cassava starch	244	338	66.73
Native palm wax	412	453	72.01
Neat cassava starch matrix	295	333	67.71
2.5% palm wax	292	331	67.30
5% palm wax	297	329	67.25
10% palm wax	299	329	66.94
15% palm wax	308	327	65.51

Table 2Glass transition, T_g and melting temperature, T_m of TPCS/palm wax.

Samples	T_g (°C)	T_m (°C)
Native cassava starch	162.9	284.5
Native palm wax	396.1	417.1
Neat cassava starch matrix	160.3	285.7
2.5% palm wax	167.5	287.1
5% palm wax	170.7	290.6
10% palm wax	169.8	289.7
15% palm wax	168.5	289.2

significantly with the addition of palm wax, which could be due to similar explanations of T_g behaviour. Thermoplastic cassava starch blends have a higher melting temperature than native cassava starch. They might be associated with good molecular hydrogen bonding interaction between palm wax, cassava starch, and plasticizer than the bonding forces in their individual native form as demonstrated by FT-IR analysis.

3.5. Tensile testing

The mechanical properties of TPCS reinforced with different palm wax concentrations were evaluated via tensile analysis at ambient temperature. Fig. 5 presents the tensile properties: (a) tensile strength, (b) tensile modulus, and (c) elongation at break, respectively. The findings revealed increments in the tensile modulus and strength with raising palm wax content from 0 to 5 wt%, respectively. The neat TPCS

showed the tensile strength and modulus were 1.27 MPa and 127.74 MPa, correspondingly. The palm wax reinforcement increment from 0 to 5 wt% had considerably improved both TPCS's tensile strength and modulus from 1.27 to 4.47 MPa and 127.74 to 345.42 MPa, respectively. Raising the content of filler from 0 to 5 wt% resulted in higher TPCS tensile strength by 251.9% increment ($p < 0.05$), while a substantial tensile modulus increment by 170% ($p < 0.05$) was evidenced at 5 wt% filler content and was greater than that of the control TPCS. Observations of increased tensile modulus and strength along with decreased elongation were also recorded. These phenomena might be associated with the advantageous interaction between TPCS and palm wax polymer matrices that expedited good interaction due to their chemical similarities and good miscibility of the starch matrix and palm wax at this filler content [34]. Besides, this might be attributed to intermolecular interaction indicated by the FTIR peak, indicating stronger interaction between the TPCS and palm wax [35,36]. Furthermore, this was also supported by the shifting peaks in the FTIR spectrum that revealed conformational changes induced by palm wax in TPCS. This led to the polymer chains' mobile difficulty, hence, raising the material's resistance to deformation. Meanwhile, the decline in E values of TPCS owing to palm wax incorporation was possibly associated with the polymer chains' movement constraint by palm wax that was in good agreement with previous works' findings [25,52]. A similar result was observed when beeswax was added into tomato pomace agro-waste, and alginate films positively affected the mechanical performance and increased the tensile strength [53].

However, further increase of palm wax at 10 wt% had significantly reduced the materials' tensile strength and modulus, contrasting to the

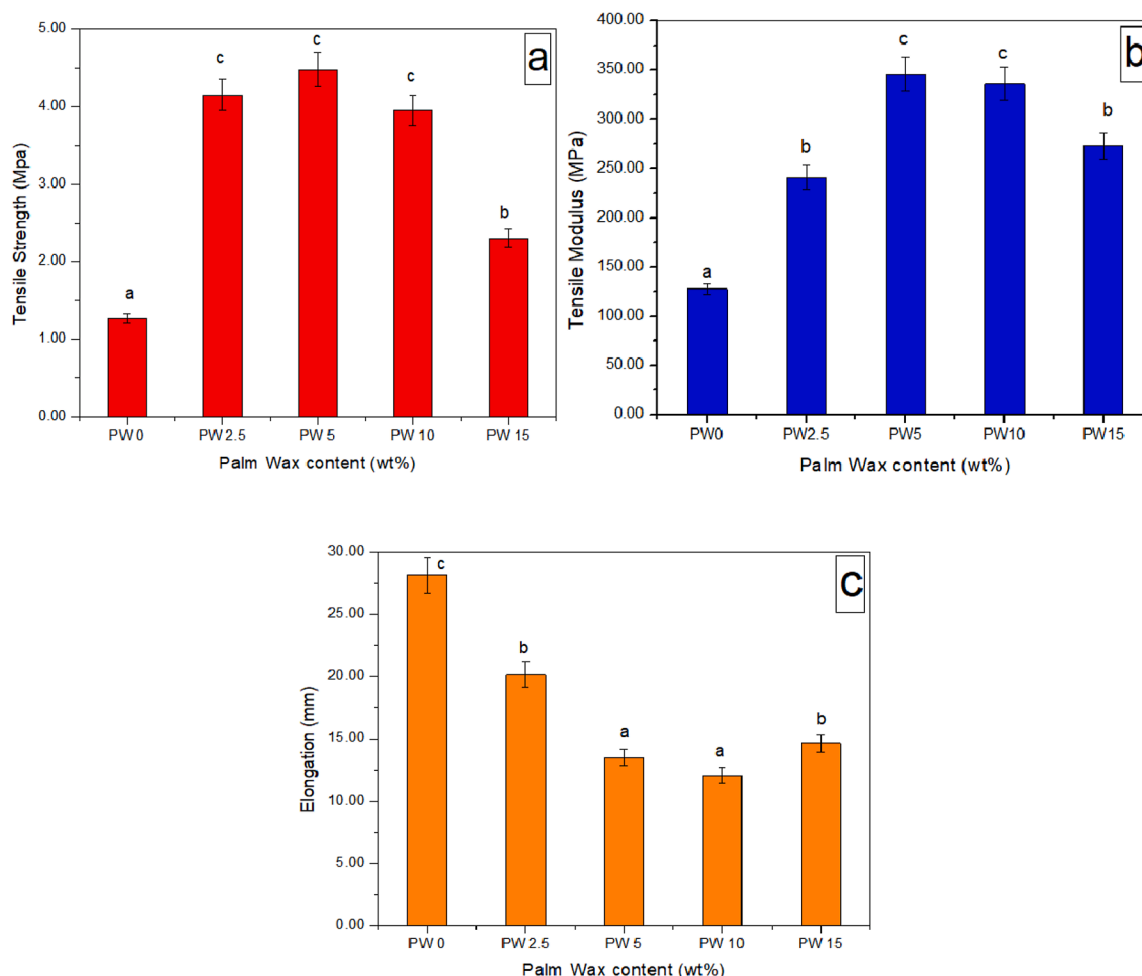


Fig. 5. (a) Tensile strength, (b) Tensile modulus, (c) Elongation at break (mm) for thermoplastic CS/palm wax.

elongation that continued to decrease significantly. These phenomena might be attributed to the matrix's discontinuity effect due to the high matrix filler content that resulted in deficit matrix-to-filler stress transfer [38,54]. A higher concentration of palm wax could result in excess replacement of the TPCS chain with weaker wax interactions. This was supported by the tensile fracture image from SEM that corresponded to the apparent gap found with higher percentage of palm wax (15 wt%) was added (Fig. 3e). This phenomenon might lead to breaks within the matrix of polymer that enabled mobility of chain throughout stretching, making the materials stiffer [55]. Therefore, as wax levels increased, samples turned out to possess more break resistance, harder, and less stretchability. Overall, the addition of palm wax in TPCS altered the starch's mechanical properties when the biopolymer contained palm wax as the filler.

3.6. Flexural testing

The flexural strength and modulus of TPCS blended with varied palm wax amounts (0 to 15 wt%) are shown in Fig. 6(a) and (b). Incorporating palm wax 0 to 5 wt% into TPCS was found to improve the flexural strength by 204.2% ($p < 0.05$) and the flexural modulus also demonstrated a rising pattern with the palm wax incorporation by 368.5% ($p < 0.05$). In sum, a comparable trend was found between flexural and tensile properties of the TPCS/palm wax, where increments in both flexural strength and modulus with increasing palm wax content in the TPCS were observed. The maximum flexural strength and modulus were exhibited by 5 wt% palm wax content; then, it tended to drop consistently with the tensile properties. Raising the filler content above 5 wt% reduced the flexural strength. The further increase in the filler content of 10 and 15 wt% yielded gradual decrements in the flexural strengths (3.57 MPa) and (1.28 MPa), respectively. Therefore, 5 wt% filler content was the optimum concentration of the wax to achieve the highest flexural strength. Significant increments in Young's modulus and flexural strength of the TPCS/palm wax might be due to a few aspects. Firstly, loadings of filler content at 5 wt% had good miscibility as a result of the better palm wax dispersion in the starch matrix at smaller concentrations. The well dispersion led to palm wax powder forming a strong interaction with the starch matrix, indicating that TPCS was suited as the matrix to the biopolymer and able to effectively transfer stress from matrix to filler. Secondly, the increased flexural strength of TPCS/palm wax, with the filler content increased up to 5 wt%, suggesting the cross-linking degree between molecular chains in the blends. The palm wax cross-linking had positively affected the elasticity modulus and flexural strength, as supported by a previous work reporting the improvement in flexural strength of corn starch incorporated with beeswax and kaolin [56]. Nevertheless, the flexural and modulus strengths of TPCS/palm wax 15 wt% (1.28 MPa and 33.48 MPa, respectively) were lower than

the TPCS/palm wax at 5 wt% (6.48 MPa and 633.87 MPa). This might be associated with the agglomerates and uneven dispersion of palm wax within the TPCS, whose palm wax failed as a reinforcing agent in TPCS. Moreover, due to the excess amount of palm wax content associated with the formation of large agglomerates and phase separation, poor distribution of particles that led to poor mechanical distribution was found, similar to the tensile results [34].

3.7. Impact testing

Fig. 7 presents the TPCS's impact strength with different contents of palm wax. It could be observed that the palm wax incorporation (0 to 5 wt%) improved its impact strength by 582.5% ($p < 0.05$). This result indicated good miscibility of TPCS, and palm wax did enhance the TPCS's ability to absorb the impact energy. Moreover, additional palm wax incorporation led to the declined impact strength. This phenomenon might be attributed to the biopolymer's flexural modulus. The materials' flexural modulus indicates their rigidity (resistance to deformation upon bending), which is critical for impact strength [57]. The decrease in impact strength at greater palm wax contents (10 to 15 wt%) could be associated with higher rigidity of the materials, which resulted in more brittle characteristics and consequently lower ability to absorb impact energy [58].

The statistical analysis of tensile, flexural, and impact tests results

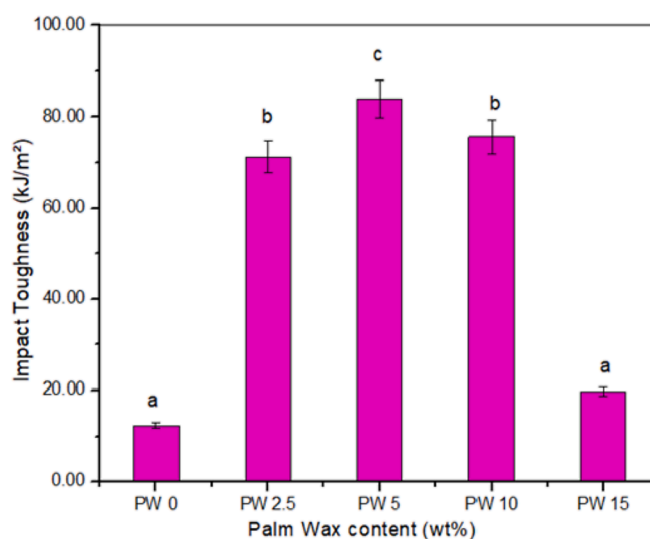


Fig. 7. Impact strength of TPCS/palm wax.

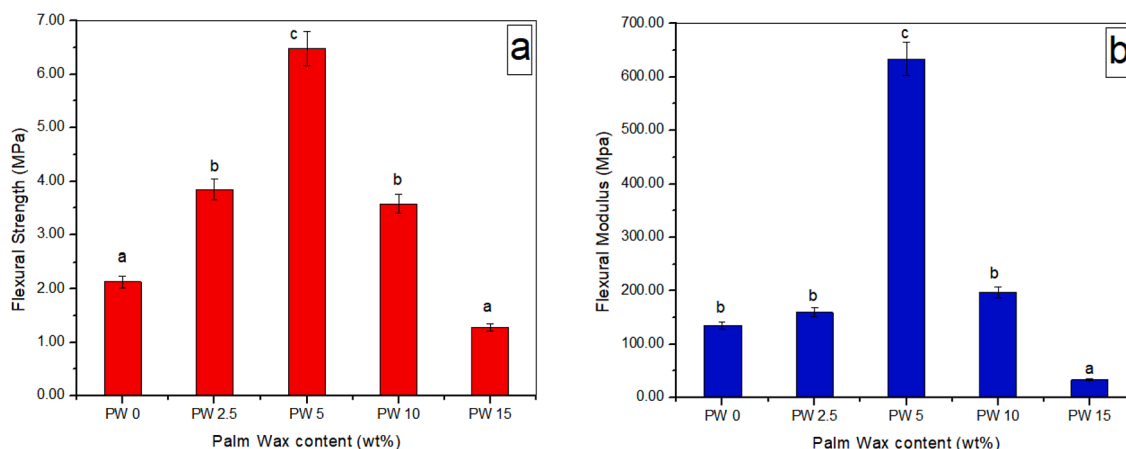


Fig. 6. (a) Flexural strength, (b) Flexural modulus of TPCS/palm wax.

were performed via one-way ANOVA, and the findings are reported in Table 3. The test's p -value was smaller than 0.05, indicating statistically significant variations in the mean values for tensile, flexural, and impact strengths of the mixtures' thermoplastic blends.

3.8. Moisture absorption

Table 4 presents the moisture absorption percentage of TPCS/palm wax throughout 11 days of storage at 25 ± 2 °C temperature and 75 ± 2% relative humidity. Customarily, all samples showed a similar rising moisture absorption pattern at the beginning of storage and declined as time increased. Generally, moisture absorption slowed after 3 days of storing and became more stable after 5 to 6 days. This result corresponded with the result of other authors who studied the moisture absorption behaviour in thermoplastic cassava starch and stated moisture stability after day 5 [59]. The incorporation of palm wax in TPCS showed improvement in its moisture barrier properties. TPCS is composed of amylopectin and amylose, whereas palm wax contains a large number of hydrophilic long-chain fatty alcohols and alkanes from the hydroxyl group interactions and oxygen bonds with water [12].

Generally, the palm wax incorporation was found to decrease TPCS samples' moisture absorption. This result showed that palm wax had positively improving the water barrier characteristic of TPCS. Hydrophobic waxes can interact with the starch network to prevent hydrogen bonds formation between water and starch molecules, therefore, reducing moisture absorption [60]. The obtained findings were parallel with previous study on the addition of beeswax to TPCS composites that significantly lowered the moisture absorption rate [61]. Furthermore, some authors found that the addition of beeswax successfully reduced the water affinity rate towards gelatin film than carnauba wax [29]. This was attributed to beeswax-based emulsions that improved the hydrophobicity to a better level in comparison with carnauba wax. Hence, it was shown in these studies that the palm wax incorporation enhanced the moisture barrier properties of the TPCS samples.

3.9. Water solubility

The water solubility of TPCS/palm wax bio-composite are presented in Fig. 8. In the present work, it was observed that the control sample's water solubility was higher than the composites due to ease of the hydroxyl groups present in the starch chain to react with water molecules [36]. Water solubility of samples with addition of palm wax in the matrix significantly ($p < 0.05$) improved water resistance with solubility value decreased from 33.82 to 23.39%, respectively. The decrement in water solubility might be associated to the existence of hydrophobic components and lipophilicity properties of palm wax in the entangled starch matrix, forming a strong starch-wax interaction network, and limiting the accessibility of hydroxyl groups interaction with introduced water. This resulted in minimized biocomposite's hygroscopic nature [36]. Also, it should be noted that the water solubility of TPCS/palm wax biocomposites reduced significantly as the palm wax content increased. Besides, palm wax is insoluble in water and when introduced into the starch matrix, it forms hydrophobic interactions that minimize the exposed binding sites [32].

A similar result was observed in the study on development beeswax into whey protein concentrate-pullulan films reduced the solubility of films, respectively [25]. Besides, several studies have shown that increasing hydrophobicity inhibits uptake of water is supported by other literatures where incorporation of palm wax into fish gelatin films

Table 3

Analysis of variance (ANOVA) summary of TPCS/palm wax.

Variables	df	Flexural strength	Flexural modulus	Tensile strength	Tensile modulus	Elongation at break	Impact strength
Mixture	4	0.00*	0.00*	0.00*	0.00*	0.00*	0.00*

* Significantly different at $p < 0.05$.

Table 4

Moisture absorption of TPCS with different amounts of palm wax.

Samples	Moisture absorption (wt%)					
	Day 1	Day 3	Day 5	Day 7	Day 9	Day 11
Neat cassava starch	10.05 ± 0.74 ^c	13.89 ± 0.63 ^d	15.33 ± 0.90 ^d	16.73 ± 0.51 ^d	16.73 ± 0.51 ^c	16.73 ± 0.51 ^c
2.5% palm wax	8.95 ± 0.92 ^b	12.26 ± 0.97 ^c	14.16 ± 0.30 ^c	14.62 ± 0.97 ^{c,d}	15.57 ± 1.37 ^{c,d}	15.57 ± 1.37 ^b
5% palm wax	7.91 ± 0.92 ^{a,b}	10.87 ± 1.09 ^b	12.88 ± 1.06 ^b	13.86 ± 1.31 ^{b,c}	14.35 ± 0.95 ^b	14.35 ± 0.95 ^b
10% palm wax	7.43 ± 0.25 ^a	10.39 ± 0.89 ^{a,b}	12.39 ± 0.41 ^{a,b}	12.86 ± 0.85 ^{a,b}	12.86 ± 0.85 ^a	12.86 ± 0.85 ^a
15% palm wax	6.92 ± 1.02 ^a	9.39 ± 0.99 ^a	11.36 ± 1.01 ^a	11.87 ± 0.96 ^a	11.87 ± 0.96 ^a	11.87 ± 0.96 ^a

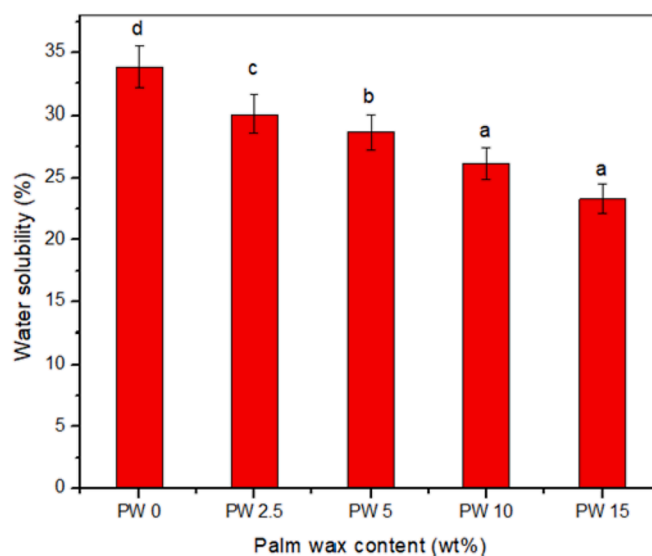


Fig. 8. Water solubility of TPCS with different amounts of palm wax.

significantly reduced the solubility from 36.06% to 15.19% respectively [32]. Meanwhile, previous study by Zhang et al. [29] on development beeswax and carnauba wax on properties of gelatin films also reported low water solubility when addition of wax into the samples. It can be concluded that the incorporation of palm wax enhanced the water resistance properties of the TPCS/palm wax bio-composite due to its hydrophobic characteristics of palm wax. Despite this observation, it was found that palm wax not only decreased water solubility but also preserved the samples' structural integrity when immersed in water.

3.10. Thickness swelling

The swelling behaviour after a 2-h immersion for TPCS/palm wax bio-composite as a function of palm wax content was shown in Fig. 9. The swelling behaviour of TPCS blends indicated similar trend with the moisture absorption behaviour. A one-way ANOVA found that the palm wax content was significantly affecting the swelling ability of the TPCS/palm wax bio-composite ($p < 0.05$). In addition, as higher concentrations of palm wax were added to the TPCS/palm wax bio-composite, swelling degree continued to decrease ($p < 0.05$), from 7.62% to

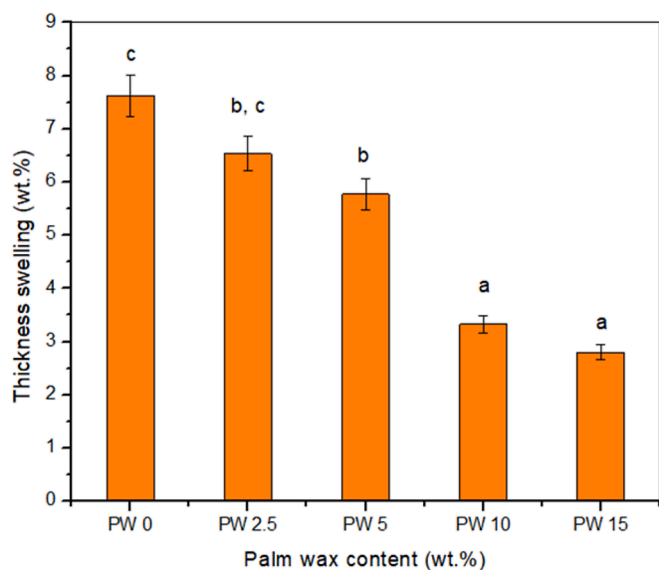


Fig. 9. Thickness swelling capacity of TPCS with different amounts of palm wax.

2.80%, indicating that the TPCS/palm wax bio-composite became more dimensionally stable after the palm wax addition. This improvement was likely due to their high hydrophobicity related to high contents in long-chain fatty alcohols and alkanes in palm wax [32]. Besides, lower swelling behaviour of the samples might be associated to the fact that lipids correspond to a fraction of solids with a lower water uptake capacity, especially palm wax, which has very hydrophobic properties [24]. Again, introduction of palm wax into TPCS leads to decrease in swelling capacity which can be associated to lower solubility capacity of palm wax as discussed in this section earlier.

These results are in accordance with the previous study on swelling ability fish gelatin films emulsified with palm wax [32]. In this study, the swelling ability of the films showed a significantly decrease with increasing palm wax concentrations from 430.41% to 201.07% for 0 to 60 wt% palm wax content. In the contrary, low swelling index are preferable for many applications because they indicate improved water resistance.

4. Conclusions

The study has demonstrated that mechanical, thermal, physical, and moisture absorption properties of TPCS were enhanced with the addition of palm wax. The results revealed that cassava starch and palm wax showed that interaction existed between these two components, and TPCS with 5 wt% palm wax exhibited the highest mechanical strength. FTIR analysis showed that adding palm wax to TPCS yielded changes in the starch's chemical composition, denoting excellent interaction between palm wax and starch. This finding also revealed the presence of a rough and irregularly fractured surface and the incorporation of palm wax has enhanced the TPCS matrix's thermal stability. Additionally, the moisture resistance of TPCS has improved with the palm wax addition, as demonstrated by the lower moisture absorption behaviour. Overall, this work has shown that the palm wax addition can improve the thermal and mechanical properties as well as reduce moisture absorption feature of TPCS. These results revealed that palm wax is an excellent candidate for the thermoplastic starch matrix's properties improvement.

CRediT authorship contribution statement

K.Z. Hafila: Conceptualization, Methodology, Investigation, Writing - Original Draft, Writing - Review & Editing, Project administration; **R. Jumaidin:** Supervision, Funding acquisition, **R.A. Ilyas:** Supervision,

Project administration, **M.Z. Selamat:** Project administration and **Fahmi Asyadi:** Project administration.

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References

- [1] K.Z. Hazrati, S.M. Sapuan, M.Y.M. Zuhri, R. Jumaidin, Extraction and characterization of potential biodegradable materials based on *Dioscorea hispida* tubers, *Polymers* 13 (2021) 584, <https://doi.org/10.3390/polym13040584>.
- [2] R.A. Ilyas, S.M. Sapuan, M.R. Ishak, E.S. Zainudin, Sugar palm nanocrystalline cellulose reinforced sugar palm starch composite: degradation and water-barrier properties, *IOP Conf. Ser. Mater. Sci. Eng.* 368 (2018), <https://doi.org/10.1088/1757-899X/368/1/012006>.
- [3] R. Jumaidin, S.M. Sapuan, M. Jawaid, M.R. Ishak, J. Sahari, Thermal, mechanical, and physical properties of seaweed/sugar palm fibre reinforced thermoplastic sugar palm starch/agar hybrid composites, *Int. J. Biol. Macromol.* 97 (2017) 606–615, <https://doi.org/10.1016/j.ijbiomac.2017.01.079>.
- [4] P. Balakrishnan, M.S. Sreekala, M. Kunaver, M. Huskić, S. Thomas, Morphology, transport characteristics and viscoelastic polymer chain confinement in nanocomposites based on thermoplastic potato starch and cellulose nanofibers from pineapple leaf, *Carbohydr. Polym.* 169 (2017) 176–188, <https://doi.org/10.1016/j.carbpol.2017.04.017>.
- [5] Y. Zhang, C. Rempel, Q. Liu, Thermoplastic starch processing and characteristics-a review, *Crit. Rev. Food Sci. Nutr.* 54 (2014) 1353–1370, <https://doi.org/10.1080/10408398.2011.636156>.
- [6] S. Karimi, A. Dufresne, P.Md. Tahir, A. Karimi, A. Abdulkhali, Biodegradable starch-based composites: effect of micro and nanoreinforcements on composite properties, *J. Mater. Sci.* 49 (2014) 4513–4521, <https://doi.org/10.1007/s10853-014-8151-1>.
- [7] K.Z. Hazrati, S.M. Sapuan, M.Y.M. Zuhri, R. Jumaidin, Effect of plasticizers on physical, thermal, and tensile properties of thermoplastic films based on *Dioscorea hispida* starch, *Int. J. Biol. Macromol.* 185 (2021) 219–228, <https://doi.org/10.1016/j.ijbiomac.2021.06.099>.
- [8] T.S. Rocha, S.G. Felizardo, J. Lin Jane, C.M.L. Franco, Effect of annealing on the semicrystalline structure of normal and waxy corn starches, *Food Hydrocoll.* 29 (2012) 93–99, <https://doi.org/10.1016/j.foodhyd.2012.02.003>.
- [9] B. Priya, V.K. Gupta, D. Pathania, A.S. Singha, Synthesis, characterization and antibacterial activity of biodegradable starch/PVA composite films reinforced with cellulosic fibre, *Carbohydr. Polym.* 109 (2014) 171–179, <https://doi.org/10.1016/j.carbpol.2014.03.044>.
- [10] S. Arun, K.A.A. Kumar, M.S. Sreekala, Fully biodegradable potato starch composites: effect of macro and nano fiber reinforcement on mechanical, thermal and water-sorption characteristics, *Int. J. Plast. Technol.* 16 (2012) 50–66, <https://doi.org/10.1007/s12588-012-9026-4>.
- [11] M.L. Sanyang, S.M. Sapuan, M. Jawaid, M.R. Ishak, J. Sahari, Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (*Arenga pinnata*) starch for food packaging, *J. Food Sci. Technol.* 53 (2016) 326–336, <https://doi.org/10.1007/s13197-015-2009-7>.
- [12] D.C. Rodrigues, C.A. Caceres, H.L. Ribeiro, R.F.A. de Abreu, A.P. Cunha, H.M. C. Azeredo, Influence of cassava starch and carnauba wax on physical properties of cashew tree gum-based films, *Food Hydrocoll.* 38 (2014) 147–151, <https://doi.org/10.1016/j.foodhyd.2013.12.010>.
- [13] E.de M. Teixeira, A.A.S. Curvelo, A.C. Corrêa, J.M. Marconcini, G.M. Glenn, L.H. C. Mattoso, Properties of thermoplastic starch from cassava bagasse and cassava starch and their blends with poly (lactic acid), *Ind. Crops Prod.* 37 (2012) 61–68, <https://doi.org/10.1016/j.indcrop.2011.11.036>.
- [14] P. Bergo, P.J.A. Sobral, J.M. Prizon, Effect of glycerol on physical properties of cassava starch films, *J. Food Process. Preserv.* 34 (2010) 401–410, <https://doi.org/10.1111/j.1745-4549.2008.00282.x>.
- [15] N. Kaisangri, O. Kerdchoechuen, N. Laohakunjit, Biodegradable foam tray from cassava starch blended with natural fiber and chitosan, *Ind. Crop. Prod.* 37 (2012) 542–546, <https://doi.org/10.1016/j.indcrop.2011.07.034>.
- [16] M. Chiumarelli, L.M. Pereira, C.C. Ferrari, C.I.G.L. Sarantópoulos, M.D. Hubinger, Cassava starch coating and citric acid to preserve quality parameters of fresh-cut "Tommy Atkins" mango, *J. Food Sci.* 75 (2010) E297–E304, <https://doi.org/10.1111/j.1750-3841.2010.01636.x>.
- [17] A.A. Curvelo, A.A. Carvalho, J.A. Agnelli, Thermoplastic starch–cellulosic fibers composites: preliminary results, *Carbohydr. Polym.* 45 (2001) 183–188, [https://doi.org/10.1016/S0144-8617\(00\)00314-3](https://doi.org/10.1016/S0144-8617(00)00314-3).
- [18] S.H.D. Hulleman, F.H.P. Janssen, H. Feil, The role of water during plasticization of native starches, *Polymer* 39 (1998) 2043–2048, [https://doi.org/10.1016/S0032-3861\(97\)00301-7](https://doi.org/10.1016/S0032-3861(97)00301-7).

- [19] J. Prachayawarakorn, P. Sangnithidej, P. Boonpasith, Properties of thermoplastic rice starch composites reinforced by cotton fiber or low-density polyethylene, *Carbohydr. Polym.* 81 (2010) 425–433, <https://doi.org/10.1016/j.carbpol.2010.02.041>.
- [20] J. Li, X. Luo, X. Lin, Y. Zhou, Comparative study on the blends of PBS/thermoplastic starch prepared from waxy and normal corn starches, *Starch* 65 (2013) 831–839, <https://doi.org/10.1002/star.201200260>.
- [21] J. Prachayawarakorn, N. Limsiriwong, R. Kongjindamunee, S. Surakit, Effect of agar and cotton fiber on properties of thermoplastic waxy rice starch composites, *J. Polym. Environ.* 20 (2012) 88–95, <https://doi.org/10.1007/s10924-011-0371-8>.
- [22] J. Prachayawarakorn, S. Chaiwatyothin, S. Mueangta, A. Hanchana, Effect of jute and kapok fibers on properties of thermoplastic cassava starch composites, *Mater. Des.* 47 (2013) 309–315, <https://doi.org/10.1016/j.matdes.2012.12.012>.
- [23] R.C.R.S. Rosa, C.T. Andrade, Effect of chitin addition on injection-molded thermoplastic corn starch, *J. Appl. Polym. Sci.* 92 (2004) 2706–2713, <https://doi.org/10.1002/app.20292>.
- [24] N.M. Hromiš, V.L. Lazić, S.L. Markov, Ž.G. Vaštag, S.Z. Popović, D.Z. Šuput, N. R. Džinić, A.S. Velićanski, L.M. Popović, Optimization of chitosan biofilm properties by addition of caraway essential oil and beeswax, *J. Food Eng.* 158 (2015) 86–93, <https://doi.org/10.1016/j.jfoodeng.2015.01.001>.
- [25] M. Khanzadi, S.M. Jafari, H. Mirzaei, F.K. Chegini, Y. Maghsoudlou, D. Dehnad, Physical and mechanical properties in biodegradable films of whey protein concentrate–pullulan by application of beeswax, *Carbohydr. Polym.* 118 (2015) 24–29, <https://doi.org/10.1016/j.carbpol.2014.11.015>.
- [26] Y. Cheng, W. Wang, R. Zhang, X. Zhai, H. Hou, Effect of gelatin bloom values on the physicochemical properties of starch/gelatin–beeswax composite films fabricated by extrusion blowing, *Food Hydrocoll.* 113 (2021), 106466, <https://doi.org/10.1016/j.foodhyd.2020.106466>.
- [27] M. Chiumarelli, M.D. Hubinger, Stability, solubility, mechanical and barrier properties of cassava starch – carnauba wax edible coatings to preserve fresh-cut apples, *Food Hydrocoll.* 28 (2012) 59–67, <https://doi.org/10.1016/j.foodhyd.2011.12.006>.
- [28] Z.H. Kamaruddin, S.M. Sapuan, M.Z. Mohamed Yusoff, R. Jumaidin, Rapid detection and identification of dioscorine compounds in *dioscorea hispida* tuber plants by LC-ESI-MS, *Bioresources* 15 (2020) 5999–6011, <https://doi.org/10.15376/biores.8.3.5999-6011>.
- [29] Y. Zhang, B.K. Simpson, M.J. Dumont, Effect of beeswax and carnauba wax addition on properties of gelatin films: a comparative study, *Food Biosci.* 26 (2018) 88–95, <https://doi.org/10.1016/j.fbio.2018.09.011>.
- [30] M. Jawaid, H.P.S. Abdul Khalil, P. Noorunnisa Khanam, A. Abu Bakar, Hybrid composites made from oil palm empty fruit bunches/jute fibres: water absorption, thickness swelling and density behaviours, *J. Polym. Environ.* 19 (2011) 106–109, <https://doi.org/10.1007/s10924-010-0203-2>.
- [31] A.A. AL-Hassan, M.H. Norziah, Effect of transglutaminase induced crosslinking on the properties of starch/gelatin films, *Food Packag. Shelf Life* 13 (2017) 15–19, <https://doi.org/10.1016/j.fpsl.2017.04.006>.
- [32] N. Syahida, I. Fitri, A. Zuriyati, N. Hanani, Effects of palm wax on the physical, mechanical and water barrier properties of fish gelatin films for food packaging application, *Food Packag. Shelf Life* 23 (2020), 100437, <https://doi.org/10.1016/j.fpsl.2019.100437>.
- [33] D. Muscat, R. Adhikari, M.J. Tobin, S. McKnight, L. Wakeling, B. Adhikari, Effect of spatial distribution of wax and PEG-isocyanate on the morphology and hydrophobicity of starch films, *Carbohydr. Polym.* 111 (2014) 333–347, <https://doi.org/10.1016/j.carbpol.2014.04.072>.
- [34] R.A. Ilyas, S.M. Sapuan, M.R. Ishak, E.S. Zainudin, Development and characterization of sugar palm nanocrystalline cellulose reinforced sugar palm starch bionanocomposites, *Carbohydr. Polym.* 202 (2018) 186–202, <https://doi.org/10.1016/j.carbpol.2018.09.002>.
- [35] R. Jumaidin, S.M. Sapuan, M. Jawaid, M.R. Ishak, J. Sahari, Characteristics of thermoplastic sugar palm starch/agar blend: thermal, tensile, and physical properties, *Int. J. Biol. Macromol.* 89 (2016) 575–581, <https://doi.org/10.1016/j.ijbiomac.2016.05.028>.
- [36] J.G. de Oliveira Filho, C.C. de O.N. Bezerra, B.R. Albiero, F.C.A. Oldoni, M. Miranda, M.B. Egea, H.M.C. de Azeredo, M.D. Ferreira, New approach in the development of edible films: the use of carnauba wax micro- or nanoemulsions in arrowroot starch-based films, *Food Packag. Shelf Life* 26 (2020), 100589, <https://doi.org/10.1016/j.fpsl.2020.100589>.
- [37] Y. Wu, F. Geng, P.R. Chang, J. Yu, X. Ma, Effect of agar on the microstructure and performance of potato starch film, *Carbohydr. Polym.* 76 (2009) 299–304, <https://doi.org/10.1016/j.carbpol.2008.10.031>.
- [38] R. Jumaidin, S.M. Sapuan, M. Jawaid, M.R. Ishak, J. Sahari, Effect of seaweed on mechanical, thermal, and biodegradation properties of thermoplastic sugar palm starch/agar composites, *Int. J. Biol. Macromol.* 99 (2017) 265–273, <https://doi.org/10.1016/j.ijbiomac.2017.02.092>.
- [39] G.F. Mehryar, K. Al-Ismael, J.H. Han, G.W. Chee, Characterization of edible coatings consisting of pea starch, whey protein isolate, and carnauba wax and their effects on oil rancidity and sensory properties of walnuts and pine nuts, *J. Food Sci.* 77 (2012) E52–E59, <https://doi.org/10.1111/j.1750-3841.2011.02559.x>.
- [40] Á.V.R. Gomes, R.H. de L. Leite, M.Q. da Silva Júnior, F.K.G. dos Santos, E.M. M. Aroucha, Influence of composition on mechanical properties of cassava starch, sisal fiber and carnauba wax biocomposites, *Mater. Res.* 22 (2019) 1–9, <https://doi.org/10.1590/1980-5373-mr-2018-0887>.
- [41] R.A. Ilyas, S.M. Sapuan, M.R. Ishak, Isolation and characterization of nanocrystalline cellulose from sugar palm fibres (*Arenga pinnata*), *Carbohydr. Polym.* 181 (2018) 1038–1051, <https://doi.org/10.1016/j.carbpol.2017.11.045>.
- [42] O.O. Oluwasina, F.K. Olaleye, S.J. Olusegun, O.O. Oluwasina, N.D.S. Mohallem, Influence of oxidized starch on physicochemical, thermal properties, and atomic force micrographs of cassava starch bioplastic film, *Int. J. Biol. Macromol.* 135 (2019) 282–293, <https://doi.org/10.1016/j.ijbiomac.2019.05.150>.
- [43] M.I.J. Ibrahim, S.M. Sapuan, E.S. Zainudin, M.Y.M. Zuhri, Preparation and characterization of cornhusk/sugar palm fiber reinforced cornstarch-based hybrid composites, *J. Mater. Res. Technol.* 9 (2020) 200–211, <https://doi.org/10.1016/j.jmrt.2019.10.045>.
- [44] M.G. Lomeli-Ramírez, S.G. Kestur, R. Manríquez-González, S. Iwakiri, G.B. de Muniz, T.S. Flores-Sahagun, Bio-composites of cassava starch-green coconut fiber: part II—structure and properties, *Carbohydr. Polym.* 102 (2014) 576–583, <https://doi.org/10.1016/j.carbpol.2013.11.020>.
- [45] Y. Cheng, W. Wang, R. Zhang, X. Zhai, H. Hou, Effect of gelatin bloom values on the physicochemical properties of starch/gelatin–beeswax composite films fabricated by extrusion blowing, *Food Hydrocoll.* 113 (2021), 106466, <https://doi.org/10.1016/j.foodhyd.2020.106466>.
- [46] S.L.M. El Halal, E. da Rosa Zavareze, M. da Rocha, V.Z. Pinto, M.R. Nunes, M. de M. de Mello Luvielmo, C. Prentice, Films based on protein isolated from croaker (*Micropogonias furnieri*) and palm oil, *J. Sci. Food Agric.* 96 (2016) 2478–2485, <https://doi.org/10.1002/jsfa.7368>.
- [47] M.L. Sanyang, S.M. Sapuan, M. Jawaid, M.R. Ishak, J. Sahari, Effect of plasticizer type and concentration on tensile, thermal and barrier properties of biodegradable films based on sugar palm (*Arenga pinnata*) starch, *Polymers* 7 (2015) 1106–1124, <https://doi.org/10.3390/polym7061106>.
- [48] J. Sahari, S.M. Sapuan, E.S. Zainudin, M.A. Maleque, Physico-chemical and thermal properties of starch derived from sugar palm tree (*Arenga pinnata*), *Asian J. Chem.* 26 (2014) 955–959, <https://doi.org/10.14233/ajchem.2014.15652>.
- [49] V. Singh, H. Okadome, H. Toyoshima, S. Isobe, K. Ohtsubo, Thermal and physicochemical properties of rice grain, flour and starch, *J. Agric. Food Chem.* 48 (2000) 2639–2647, <https://doi.org/10.1021/jf990374f>.
- [50] M. Mitrus, Glass transition temperature of thermoplastic starches, *Int. Agrophys.* 19 (2005) 237–241.
- [51] R.A. De Graaf, A.P. Karman, L.P.B.M. Janssen, Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing, *Starch* 55 (2003) 80–86, <https://doi.org/10.1002/star.200390020>.
- [52] J. Prachayawarakorn, P. Ruttanabus, P. Boonsom, Effect of cotton fiber contents and lengths on properties of thermoplastic starch composites prepared from rice and waxy rice starches, *J. Polym. Environ.* 19 (2011) 274–282, <https://doi.org/10.1007/s10924-010-0273-1>.
- [53] G. Tedeschi, J.J. Benitez, L. Ceseracciu, K. Dastmalchi, B. Itin, R.E. Stark, A. Heredia, A. Athanassiou, J.A. Heredia-Guerrero, Sustainable fabrication of plant cuticle-like packaging films from tomato pomace agro-waste, beeswax, and alginate, *ACS Sustain. Chem. Eng.* 6 (2018) 14955–14966, <https://doi.org/10.1021/acssuschemeng.8b03450>.
- [54] M. Omar-Aziz, F. Khodaiyan, M.S. Yarmand, M. Mousavi, M. Gharaghani, J. F. Kennedy, S.S. Hosseini, Combined effects of octenylsuccination and beeswax on pullulan films: water-resistant and mechanical properties, *Carbohydr. Polym.* 255 (2021), 117471, <https://doi.org/10.1016/j.carbpol.2020.117471>.
- [55] M. Chiumarelli, M.D. Hubinger, Evaluation of edible films and coatings formulated with cassava starch, glycerol, carnauba wax and stearic acid, *Food Hydrocoll.* 38 (2014) 20–27, <https://doi.org/10.1016/j.foodhyd.2013.11.013>.
- [56] S. Polat, M.-K. Uslu, A. Aygün, M. Certel, The effects of the addition of corn husk fibre, kaolin and beeswax on cross-linked corn starch foam, *J. Food Eng.* 116 (2013) 267–276, <https://doi.org/10.1016/j.jfoodeng.2012.12.017>.
- [57] M. Jawaid, H.P.S. Abdul Khalil, A. Abu Bakar, Woven hybrid composites: tensile and flexural properties of oil palm-woven jute fibres based epoxy composites, *Mater. Sci. Eng. A* 528 (2011) 5190–5195, <https://doi.org/10.1016/j.msea.2011.03.047>.
- [58] F. Vilaseca, J.A. Mendez, A. Pèlach, M. Llop, N. Canigual, J. Gironès, X. Turon, P. Mutjé, Composite materials derived from biodegradable starch polymer and jute strands, *Process Biochem.* 42 (2007) 329–334, <https://doi.org/10.1016/j.procbio.2006.09.004>.
- [59] H. Ibrahim, M. Farag, H. Megahed, S. Mehanny, Characteristics of starch-based biodegradable composites reinforced with date palm and flax fibers, *Carbohydr. Polym.* 101 (2014) 11–19, <https://doi.org/10.1016/j.carbpol.2013.08.051>.
- [60] D. Kowalczyk, M. Kordowska-Wiater, B. Solowiej, B. Baraniak, Physicochemical and antimicrobial properties of biopolymer-candelilla wax emulsion films containing potassium sorbate – a comparative study, *Food Bioprocess Technol.* 8 (2015) 567–579, <https://doi.org/10.1007/s11947-014-1423-6>.
- [61] Z.N. Diyana, R. Jumaidin, M.Z. Selamat, M.S.M. Suan, Thermoplastic starch/ beeswax blend: characterization on thermal mechanical and moisture absorption properties, *Int. J. Biol. Macromol.* 190 (2021) 224–232, <https://doi.org/10.1016/j.ijbiomac.2021.08.201>.