A comparative study on chitosan/gelatin composite films with incorporated Pith and Cortex of Napier Grass.

T.N. Tuan Rohadi², M.J.M. Ridzuan¹*, M.S. Abdul Majid¹, E.M. Cheng², M.J. Norasni³, Noraini Marsi⁴

¹Faculty of Mechanical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
²Faculty of Electronic Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
³Department of Mechanical Engineering, Politeknik Ungku Omar (PUO), Jalan Raja Musa Mahadi,31400 Ipoh Perak, Malaysia
⁴Department of Mechanical Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 84600 Panchor, Johor, Malaysia

*Corresponding Author: ridzuanjamir@unimap.edu.my

Abstract. The problem in end-of-life of petroleum-based plastic management had risks wildlife and human health with rapid used in fossil reserves. Therefore, the exploration of biodegradable plastics that embraced a new eco-friendly alternative to overcome these limitations have been conducted. In this paper, the chitosan and gelatine composite film with incorporated pith and cortex of Napier grass were prepared via solution casting will be evaluated. The thermal, chemical, mechanical properties and morphological characterization of composite film had been conducted via thermo-gravimetric analysis, Fourier transforms infrared spectroscopy, tensile strength, and scanning electron microscope. The results shows that the cortex had potential to be used as reinforcement material same as the pith to broaden the use of Napier grass in industrial. Thus, further studied with additional of cellulose from pith and cortex of Napier grass in the chitosan/gelatine composite films may improve the tensile strength due to the removal of non-cellulosic component.

1. Introduction

Petroleum-based plastic is suit to be used for different type of storing and packaging [1]. However, the used of petroleum-based plastic could cause plastic pollution. This is because the petroleum-based plastic had been dumped into the landfill and rarely be recycled every year [1]. Furthermore, huge consumption of petroleum-based plastic has depleted rapidly the petroleum reserves [1]. Therefore, the exploration of biodegradable plastics that embraced a new eco-friendly alternative to overcome these limitations have been conducted. This can reduce the decay time and the long-term cost especially if the clean-up costs from plastic pollution are added in the calculation. The chitosan and gelatine can be classified as renewable materials, thus promoting their application in food packaging [1]. Nevertheless, it is well known that stand-alone chitosan or gelatine films are brittle and susceptible to
cracking due to the polymer’s resilient cohesive energy density [2]. Therefore, several researchers have tried to improve the film properties by blending gelatine and chitosan with other high strength polymers [1]. The use of natural fibres is a great benefit as it is environmentally friendly, stable, sustainable, biodegradable, renewable and excellent mechanical properties [3]. Nonetheless, most of natural fibres are costly and in short supply due to scarcity of natural resources such as woods and cotton [3]. Therefore, these have led to another further research to find new composite film from agriculture such as banana [4], oil palm [5] and durian [6]. Among the agricultural produce, Napier grass stem (NS) is a potential candidate as its stem can be divided into two main part, which are pith and cortex of NS. Each represents 16 and 84% of NS dry weight, respectively [7]. Yet, the researcher only attracted to investigate the pith part despite the high percentage content in the cortex part of NS is high [8]. In previous papers, Senthil Muthu Kumar et al. had designed composite films using cotton linter pulp as matrix and treated cellulose from the pith of NS with 80 % of acetic acid [8]. Apparently, this is the first investigation for characterization of the thermal, chemical composition, mechanical properties and morphological of chitosan/gelatine composite films with incorporated pith and cortex of NS. Therefore, this comparison study of the chitosan/gelatine composite films with incorporated pith and cortex of NS were subjected using thermo-gravimetric analysis (TGA), Fourier transforms infrared (FTIR) spectroscopy, tensile strength and scanning electron microscopy (SEM). This can provide a new information for broadening the use of NS.

2. Methodology

2.1. Material Preparation
The NS originates from Asia tropical and can be located in northern peninsular Malaysia. The process of the removal of residue and wax at the NS were done by cutting it into 4-6 cm, crushed and submerged in water for 2 months. Subsequently, the soaked NS were washed under tap water for five times before it was dried for 2 days in a room temperature. The separated pith and cortex of NS was prepared using the method based on previous literatures [7]. The total weight of each NS was measured and the recorded ratio of the cortex to pith of NS was 4:21. Generally, if the total weight of each NS was measured using an analytical balance is 150g, then the pith and cortex will be separated as 24 and 126g, respectively. The separated dried pith and cortex of NS were grounded and sieved several times to prepare uniform size of powder form.

2.2. Composite Films Preparation
The composite film was prepared via solution casting method by mixing the chitosan and gelatin solution. Primarily, the chitosan powder was dissolved in 100 ml of 2 % (v/v) acetic acid for 12 hours to prepare the chitosan solution. Secondly, the gelatin powder was dissolved in 100 ml water for 30 min to prepare the gelatin solution. Subsequently, 1 wt. % of PNS and CNS was mixed separately in 40 and 60 mL of the gelatin solutions and chitosan solution, respectively for 1 hours. Consequently, 0.5 mL of glycerol was added and stirring process continued for 24 hours. Finally, 30 mL of composite film solutions were poured into the glass petri dishes and dried for 1 day before peeled it off. The chitosan/gelatin composite films with incorporated PNS and CNS were prepared.

2.3. Sample Characterization
The chitosan/gelatin composite films with incorporated PNS and CNS were evaluated based on thermal, chemical composition, mechanical properties and morphological properties using a TGA, FTIR, Universal testing machine (UTM), and SEM, respectively. The flow rate of flowing nitrogen (N₂) atmosphere, heating rate and temperature range for TGA were set as 10 mL/min, 10 °C/min and 37 to 600 °C, respectively. The FTIR spectroscopy were conducted in 32 scans per sample and 4 cm⁻¹ spectral resolution. The scanning images were obtained by using an acceleration voltage of 5 kV and magnification of 1000×. Tensile strength tests were performed to evaluate the mechanical properties of
the composite films according to the ASTM D882-12 standard. The crosshead speed was fixed at 2 mm/min. The tensile strength test was repeated five times to obtain an average tensile strength value. The tensile strength was determined using the following equation [4]:

\[
\text{Tensile strength} = \frac{\text{Load (N)}}{\text{Area of sample thickness}} \tag{1}
\]

3. Results and Discussion

3.1. Thermo-gravimetric analysis (TGA)

The TGA result for chitosan/gelatin composite films with incorporated PNS and CNS were presented in Fig. 1. From Fig. 1, the composite films with incorporated PNS had the highest final residues (21.75%) while incorporated CNS had the lowest final residues (13.45%). This indicates that the mass loss was dependent on the type of fibre which may affect the interaction between NS, chitosan, and gelatine [7]. This also shows that the chitosan/gelatin composite films with incorporated PNS can resist thermal degradation at high temperatures compared to incorporated CNS. In addition, final residue formation is caused by the composite film residue after decomposition of moisture, hemicellulose, cellulose and lignin [8]. This was suspected due to the cortex have higher lignin content (18.5%) than the pith (15.5%) [4]. Therefore, PNS and CNS has shows the potential as reinforcing material for composite film fabrication, which is beneficial to the environment.

![Fig. 1. TGA curves for the chitosan/gelatin composite films with incorporated PNS and CNS.](image)

3.2. Fourier transforms infrared spectroscopy (FTIR)

The FTIR spectra of the chitosan/gelatin composite films with incorporated PNS and CNS were presented in Fig. 2. Based on Fig. 2, it can be observed the presence of acetyl ester or carbonyl aldehyde groups of lignin and hemicellulose at the 1089 cm\(^{-1}\) band, which are related to the C–C stretching in the composite film [10]. Besides, the peaks at 3270 cm\(^{-1}\) show that the chitosan/gelatin composite films with incorporated PNS had more stable and stronger hydrogen bonding compared to CNS [11]. Overall, Table 1 had concluded the existed of four major band position for absorption peaks in the composite film was successfully demonstrated the bio-renewable composite film fabrication [11].

3.3. Mechanical properties

The tensile strengths of the chitosan/gelatin composite films with incorporated PNS and CNS are presented in Fig. 3.
Table 1. Peak absorption involved at different band position existed in the samples.

| Band position (cm$^{-1}$) | Involved group                                                                                                                                 |
|---------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| 3260–3390                 | Hydroxyl group (O–H) absorption peak of the carbohydrate structure [11]. Stretching vibrations of pendant groups existed [1]                   |
| 2910–2940                 | The CH$_2$ symmetrical bending vibration may change the crystallinity of fibre [11]. C–H stretching vibrations in the chitosan chain [8].         |
| 1630–1644                 | Adsorption of water [8]. Peaks of the C=O and C=C bonds [8].                                                                                  |
| 1030–1041                 | The C–O bending of the C–O–H group and C–O–C stretching linkage of polysaccharide chains [1].                                               |

![FTIR graph](image1)

**Fig. 2.** FTIR for the chitosan/gelatin composite films with incorporated PNS and CNS.

![Tensile strength graph](image2)

**Fig. 3.** The tensile strengths of the chitosan/gelatin composite films with incorporated PNS and CNS.

From Fig. 3, the tensile strengths of the chitosan/gelatin composite films with incorporated PNS and CNS are $0.95 \pm 0.228$ and $0.54 \pm 0.056$ MPa, respectively. This shows that the composite films
with incorporated pith had the highest tensile strength. This is because the homogenous distribution of filler can affect the mechanical strength of composite film [4]. In addition, addition of glycerol in the combination of fibre, chitosan, and gelatine had formed a stronger –OH interactions between the material and glycerol [12]. Moreover, this also shows that the addition of PNS and CNS had improved the flexibility and reduce the stiffness of the composite film. According to previous studies, gelatine- and chitosan-based composite film are brittle and susceptible to crack owing to the resilient cohesive energy density of the polymer [1]. Furthermore, Talja et al. had proposed that the trend of the tensile strength gradually increase with the additional of cellulose as fillers [11]. Therefore, based on these results, further research on additional of cellulose from PNS and CNS in the chitosan/gelatine composite films may improve the tensile strength to sustain a high load in various application.

3.4. Scanning electron microscope (SEM)
The surface morphology for the chitosan/gelatin composite films with incorporated PNS and CNS were shown in Fig. 4. From the SEM results, it can be seen that there are difference in surface morphology for the chitosan/gelatin composite films with incorporated PNS and CNS. These micrographs also showed that the surface features consists of granules, filler-pulled-out propagations, small white particles and impurities such as hemicellulose and lignin [13]. This indicates the lack of a solvent interaction or the gelatine/chitosan is not fully gelatinised during the composite film production process [14]. Both composite films show a poor interfacial adhesion and present of some voids on the surface morphology, along with groove surfaces. Thus, this may result in poor mechanical properties for the composite film [14]. However, the presence of some small pores can facilitate interactions with microbes and increase the biodegradation rate [15].

![Fig. 4. SEM for the chitosan/gelatin composite films with incorporated (a) cortex and (b) pith of NS.](image)

4. Conclusions
The thermal, chemical composition, mechanical properties and morphology of the chitosan/gelatin composite films with incorporated PNS and CNS were analyzed. There was different result in the chitosan/gelatin composite films with incorporated PNS and CNS. The result shows a successful production of the bio-renewable composite film due to the present of four major band position for O–H, C–H, C=O, and C–O absorption peaks. Moreover, the addition of PNS and CNS had improved the flexibility and reduce the stiffness of the composite film. The results in poor mechanical properties had agreed with FTIR, TGA, and microscope results due to the presence of lignin and hemicellulose in the composites film. Therefore, based on these results, the further research on additional of cellulose from PNS and CNS in the chitosan/gelatin composite films may improve the tensile strength while achieve the aim of broadening the use of NS.
Acknowledgements
This work is financially supported by centre of the Fundamental Research Grant Scheme from Ministry of Education, Malaysia (Ref: FRGS/1/2020/STG05/UNIMAP/02/1). The analysis was conducted at Universiti Malaysia Perlis (UniMAP) and Universiti Teknologi Mara (UiTM) Shah Alam. The authors also gratefully thank the Politeknik Ungku Omar (PUO), and Universiti Tun Hussein Onn Malaysia (UTHM) for the technical assistance in conducting this research.

References
[1] Kumar S, Shukla A, Baul P P, Mitra A and Halder D 2018 Biodegradable hybrid nanocomposites of chitosan/gelatin and silver nanoparticles for active food packaging applications Food Packag. Shelf Life 16 178–84
[2] Kumar S, Singh P, Gupta S K, Ali J and Baboota S 2020 Biodegradable and Recyclable Packaging Materials: A Step Towards a Greener Future Encyclopedia of Renewable and Sustainable Materials (Elsevier) pp 328–37
[3] Subramanian K R and Labs T 2018 The Crisis of Consumption of Natural Resources Int. J. Recent Innov. Acad. Res. 2 8–19
[4] Heri Hermansyah, Rena Carissa, Merisa Bestari Faiz and Priscilla Deni 2014 Food Grade Bioplastic Based on Corn Starch with Banana Pseudostem Fibre/Bacterial Cellulose Hybrid Filler Front. Chem. Eng. Metall. Eng. Mater. III 997 158–68
[5] Rasila S, Rasli A M, Ahmad I, Lazim A M and Hamzah A 2017 Extraction and characterization of cellulose from agricultural residue-Oil Palm Fronds Malaysian J. Anal. Sci. 21 1065–73
[6] Koay S C, Subramanian V, Chan M Y, Pang M M, Tsai K Y and Cheah K H 2018 Preparation and Characterization of Wood Plastic Composite Made Up of Durian Husk Fiber and Recycled Polystyrene Foam. ed S Narayana Namasivayam, M Hosseini Fouladi, S W Eunice Phang, B L Chua, Y H Chow, L C Yong and A S M Al-Obaidi MATEC Web Conf. 152 02019
[7] Prinsen P, Gutiérrez A and del Río J C 2012 Lipophilic Extractives from the Cortex and Pith of Elephant Grass (Pennisetum purpureum Schumach.) Stems J. Agric. Food Chem. 60 6408–17
[8] Senthil Muthu Kumar T, Rajini N, Obi Reddy K, Varada Rajulu A, Siengchin S and Ayrlimus N 2018 All-cellulose composite films with cellulose matrix and Napier grass cellulose fibril fillers Int. J. Biol. Macromol. 112 1310–5
[9] Maulida, Siagian M and Tarigan P 2016 Production of Starch Based Bioplastic from Cassava Peel Reinforced with Microcrystalline Cellulose Avicel PH101 Using Sorbitol as Plasticizer J. Phys. Conf. Ser. 1742–6596
[10] Lubs M, Bangun Harahap M, Hendra M, Ginting S, Sartika M and Azmi H 2018 Production of Bioplastic from Avocado Seed Starch Reinforced With Microcrystalline Cellulose from Sugar Palm Fibers J. Eng. Sci. Technol. 13 381–93
[11] Muhammad A, Roslan A, Sanusi S N A, Shahimi M Q and Nazari N Z 2019 Mechanical properties of bioplastic form cellulose nanocrystal (CNC) mangosteen peel using glycerol as plasticizer J. Phys. Conf. Ser. 1349 12099
[12] Marichelvam, Jawaid and Asim 2019 Corn and Rice Starch-Based Bio-Plastics as Alternative Packaging Materials Fibers 7 32
[13] Ridzuan M J M, Abdul Majid M S, Afendi M, Aqmariah Kanafiah S N, Zahri J M and Gibson A G 2016 Characterisation of natural cellulosic fibre from Pennisetum purpureum stem as potential reinforcement of polymer composites Mater. Des. 89 839–47
[14] Amin M R, Chowdhury M A and Kowser M A 2019 Characterization and performance analysis of composite bioplastics synthesized using titanium dioxide nanoparticles with corn starch Heliyon 5 e02009
[15] Rohmawati B, Nata Sya’idah F A, Rhismayanti, Alighiri D and Tirza Eden W 2018 Synthesis of Bioplastic-based Renewable Cellulose Acetate from Teak Wood (Tectona grandis) Biowaste Using Glycerol-Chitosan Plasticizer Orient. J. Chem. 34 1810–6