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Influence of cellulose II polymorph nanowhiskers on bio-based nanocomposite film from Jatropha oil polyurethane

S O A SaifulAzry1*, T G Chuah1*, M T Paridah1, M M Aung2*, M A Ridzuan1, C H Lee1*, S Sariah1, S H Lee1 and A H Juliana3

1 Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor, Malaysia
2 Faculty of Engineering, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia
3 Faculty of Technology Management and Business, Universiti Tun Hussein Onn, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

* Authors to whom any correspondence should be addressed.

E-mail: saifulazry@upm.edu.my, chuah@upm.edu.my and lee_seng@upm.edu.my

Abstract

Green polyurethane from plant oil-based such as Jatropha oil has recently received attention due to its environmental friendliness and sustainability. With incorporation of nanocellulose even though at low loadings in polymer matrices has shown a significant improvement. However, limited research has been done on different cellulose nanowhisker (CNW) polymorphs and their impact on composites. A number of studies have shown that the handling of cellulose polymorph also improves the properties of composite products as the cellulose II is more chemically reactive and thermodynamically stable than cellulose I. The aim this study is to investigate the effect of CNW with cellulose II polymorph in Jatropha oil-based polyurethane (JOPU). Different weight percent of CNW-II (0.1–1.5 wt%) were incorporated into JOPU films using vacuum rotavap and film casting. The total weight of 6 g was used as a fixed ratio (1:3) matrix of 4,4’-diphenyl-methane disocyanate (MDI) and Jatropha-oil polyol (JO). The acid hydrolysis process was subjected to mercerised microcrystalline cellulose (MMC) for the production of CNW-II. X-ray diffraction analyses were carried out to confirm cellulose II lattice of CNW-II. The CNW-II morphology was analysed using the transmission electron microscope. It was found that CNW-II had a granule-like shape with an average size of 74.04 nm in length and 21.36 nm in width. The translucency and colour of the film have also been tested by optical light microscopes. The clarity of the film and colour found affected by the highest CNW-II film loading. Based on the FTIR analysis, the spectra of all films show a typical polyurethane pattern that JOPU spectra found dominant due to very low volume NCW-II content in film. The same trend is observed for thermal degradation tested using a thermogravimetric analyser. Tensile strength and water uptake have been shown to increase in proportion to the CNW-II content.

1. Introduction

Cellulose consisting of β-1,4-linked chains of D-glucopyranose and being an active chemical due to the presence in each glucose unit of the three hydroxyl groups. These groups of hydroxyl are primarily responsible for cellulose reactions, or so-called reactivity. Its structures and properties remain intriguing despite many years of study. In general, four different cellulose polymorphs are classified with additional subclasses, including cellulose I, II, III and IV [1]. Cellulose I (also referred to as native cellulose) and II are the most studied types in which cellulose I generally exhibits better mechanical properties, while cellulose II provides better functionality [2, 3]. Mercerisation and regeneration of cellulose from solution are the most common method of transforming cellulose I into cellulose II polymorph and is irreversible once they have been transformed. The difference in arrangement of its lattice between cellulose I and cellulose II. Cellulose II is packed against parallel, while the chains run in parallel in cellulose I. The packing structure indirectly makes cellulose II is more chemically

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reactive and thermodynamically stable than cellulose I [2, 4]. The exploitation of different cellulose polymorphs already used in the industry but mainly used in the textile industry to improve textile finishing and quality (e.g. rayon) and packaging film (e.g. cellophane). However, a number of studies have shown that the handling of cellulose polymorph also improves the properties of composite products [5–9].

Nanocellulose materials (i.e. cellulose nanowhisker/nanocrystals, cellulose nanofibrils, bacterial nanocellulose) were progressively studied in particular for multifunctional nanomaterials with singular and adjustable properties for various applications such as reinforcement materials, biomedicine, food additives, electronics, packaging, biosensors, water treatment, etc. [10, 11]. Nanocellulose exhibits remarkable features, such as large surface area, high mechanical properties, high aspect ratio, biodegradability, and reactive groups that could potentially be modified/functionalyzed [3, 12, 13]. Incorporation of nanocellulose into polymer matrices, although a significant improvement in mechanical strength has been demonstrated at low loadings [14–16]. Depending on the source and production method, nanocellulose varied in its inherent properties (i.e. physical, morphological, mechanical, dimensional) [17]. For cellulose nanowhiskers, it contains high crystalline cellulose and is mostly derived from plant-based fibres. Cellulose nanowhiskers are produced by the process of acid hydrolysis and sulphuric acid is the most commonly used acid due to its highly stable aqueous suspension [18]. It has protonated cyclic oxygen or glucosidic oxygen and dissolved glucosidic bonds, especially in the amorphous region of the cellulose chain. This process breaks cellulose into shorter chain fragments by retaining the crystalline region and preferably hydrolysing the amorphous domains [19]. The remaining crystalline area preserves the core nature of the polymer chain and contains esterification (sulfonation) of hydroxy (−OH) group of polymer chain. The CNW generally has a high aspect ratio (3–5 nm wide, 50–500 nm length) in pattern like whiskers [19].

In terms of cellulose morphological studies, most of the work focuses on macro/micro cellulose fibre and is very limited to nanoscale cellulose materials, particularly cellulose nanowhiskers [2]. A study conducted by [20] comparing cellulose I and cellulose II nanocrystal and its effects on composites showed promising findings and worth exploring.

Jatropha curcas L. oil is one of the plant-based polyurethane production sources. It originates from tropical America and is easy to find in tropical and sub-tropical America, Africa and Asia [21, 22]. Malaysia is home to about 600,000 acres of Jatropha plantations and a large number of nurseries and collective centres [21]. In order to produce Jatropha oil (JO) at relatively low cost, Jatropha fruit seeds are employed [22]. It contains 78.9% unsaturated fatty acids, primarily linoleic acid (34.4%) and oleic acid (43.1%) [23]. Intensive research work has therefore been done on the production of Jatropha oil-based polyurethane (JOPU) [24, 25]. Plant oil-based polyurethane, on the other hand, has recently received attention due to its environmental friendliness and sustainability, as well as its feasible use routes. In addition, the fluctuation in the price of crude oil, sustainability issues and environmental concerns of conventional polyurethane resin are highly affected. Green polyurethane was then rapidly transformed into an alternative source, which was more price stable [26]. However, plant-oil-based polyurethanes has its own drawbacks such as deficiencies in mechanical properties, water resistance, and thermal stability limit the practical its’ application [27]. Thus, by introduction of nano-materials such as nanocellulose could improve these drawbacks, and this strategy has become a current research hotspot [27].

As described earlier, limited research has been done on different cellulose nanowhisker polymorphs and their impact on composites. Our previous work [28] was a study of native CNW in Jatropha oil-based polyurethane bionanocomposite film. The comparison between native and mercerised cellulose also took place in our previous work [29]. Since the cellulose II is more chemically reactive and thermodynamically stable than cellulose I as mentioned earlier, by incorporating CNW–II in JOPU is expected to improve the properties of this bio-based nanocomposite films. Thus, the aim this study is to investigate the effect of CNW with cellulose II polymorph in Jatropha oil-based polyurethane (JOPU) Since the this study will continue to focus on the use of cellulose II CNW with specific loading contents. The aim of the research is to investigate the results of the introduction of CNW cellulose II in JOPU. The physical, mechanical, thermal and water absorption properties of the film were studied and discussed.

2. Methodology

2.1. Materials

Mercerised microcrystalline cellulose (MMCC) was produced from commercial softwood pulp-based microcrystalline cellulose. The mercerisation process was described in detail in our previous study [29] and used in the processing of cellulose II nanowhiskers (CNW-II) in this research. Biofuel Bionas Sdn Bhd, Kuala Lumpur, Malaysia has been supplied with crude Jatropha oil (JO) and used as received. On the other hand, the chemicals used for CNW-II insulation and Jatropha oil-based polyol were reagent grades supplied by R&M Chemicals, Malaysia. Potassium hydroxide, sodium hydroxide, pyridine, phthalic anhydride, potassium
hydrogen phthalate, acetone, chlorobenzene, hydrogen bromide, magnesium sulphate anhydrous, sodium bicarbonate, sulfuric acid (95%–98%), methanol, hydrogen peroxide 30%, and formic acid 98% are the chemicals used in this study. Dimethylformamide (DMF) as an organic solvent and 4,4′-diphenyl-methane diisocyanate (MDI) was used to produce polyurethane film, purchased from Systerm, Malaysia

2.2. Isolation of cellulose nanowhiskers

The solution of sulfuric acid (64 wt%) has been preheated to 45 °C and is blended with the MMCC. There is 1:10.0 g mL⁻¹ of acid in the MMCC ratio. The blend was then vigorously agitation for 60 min washing with 6000 RPM centrifugation for 10 min and 30 min during the following cycles to remove the acid solution from the hydrolysed cellulose mixture, until a cloudy suspension is observed. The dialysis membrane is then dialysed until the neutral pH is reached. Finally, the CNW-II was freeze-dried using VirTis BenchTop Pro Freeze Dryer at −50 °C and 0.05 mbar for period of 1–3 days.

2.3. Synthesis of Jatropha oil-based polyol

Polyol was synthesized by epoxidation and hydroxylation using method from our earlier works [20, 21]. The JO was poured into a four-necked bottomed flask with formic acid which was agitated at 40 ºC. Then 30% of the peroxide of hydroxide was added by dropwise for 30 min into the mixture. For 2 h, 60 ºC temperature was kept and cooled to room temperature. The aqueous layer was removed and the oil layer or epoxidizing Jatropha oil (EJO) was then repeatedly washed using distilled water containing magnesium sulphate as a drying agent to eliminate excess acid. The formic acid catalyst, distilled water and methanol was added to the four-neck round-bottomed flask and heated to 64 ºC. The EJO was then added to the mixture and stirred for 25 min. Hydroxylation was performed using a 10:9:1 ratio (EJO: methanol: distilled water). This washed mixture with 10 ml of distilled water and left after shaking for 30 min. The underlying aqueous layer was discarded and the remaining water and methanol was removed using vacuum rotary evaporator for two hours which produce clear golden JO polyol.

2.4. Production of nanocomposite films

The loadings of CNW-II are 0.1, 0.25, 0.5, 1.0, and 1.5 wt%. The CNW-II was first mixed in 35 ml of DMF solvent and dispersed for 30 min in IKA Ultra Turax 10 homogenizer. As film matrix, 6 g of JO polyol and MDI (3:1 ratio) were used. The JO polyol and CNW-II were placed at 70 ºC on a vacuum rotary evaporator for about 50–75 min for stable suspension. The suspension then poured into the teflon petri dish and cured with a one-hour vacuum condition oven at 70 ºC, then continues for 23 h at atmospheric pressure. The cured film was then conditioned to complete curing in a desiccator for seven days at room temperature (50% RH). The films averaged 0.25 mm thick.

2.5. Characterisation

2.5.1. Microscopy and physical examination

The specimens CNW-II were investigated using Hitachi Model H-7100 transmission electron microscope (TEM). The scanning electron microscope (SEM) Hitachi S-3400N was used to analyse MMCC fibres and Jeol JSM 7600 F Field Emission Scanning Electron Microscopy (FE-SEM) for surface morphology of films. Optical translucency and composite colour film samples were investigated under an optical light microscope (Olympus model SZX12) and connected to the software of the CellA digital image analyser. The images were captured at 2.5 magnifications. The density of specimen films was determined by Metler Toledo, an electronic densimeter model XS205DU, with average 3 specimens for each film type.

2.5.2. FTIR and X-ray diffraction analysis.

The data for the FTIR spectra of films were collected using a Perkin-Elmer Spectrum 2000, fitted with a horizontal germanium attenuated total reflectance (ATR) accessory. The spectra were recorded between 4000 and 500 cm⁻¹ with a nominal resolution of 4 cm⁻¹. X-ray diffraction analyses for MMCC and CNW-II were performed using the IS/APD2000 X-ray diffractometer. In step scan mode, the pattern of diffraction was collected with an angle between 5 and 30°. The wavelength of the source of Cu/Ka radiation was 1.5405 Å. The spectra were produced at 30 mA with an acceleration voltage of 60 kV. The data was analysed using the XPert HighScore software. The crystalline index (CI, %) of the samples was calculated as follows:

$$CI\% = \frac{[I_c/(I_c + I_a)]}{100}$$

Where, Ic and Ia represent the intensity of the lattice peak diffraction and the amorphous regions, respectively [1].
2.5.3. Thermal characterisation
A TGA Q500-TA instrument was used to study the thermogravimetric analysis (TGA) of specimens with a heating rate of 10 °C/min out in the atmosphere of nitrogen. Temperature scanning of the analysis from room temperature up to 600 °C.

2.5.4. Mechanical and water uptake characterisation
The INSTRON universal Testing Machine was used to study the mechanical properties of specimens in accordance with standard ASTM D638–03. Sample films have also been analysed for their water uptake using method adopted from previous work [22, 28]. The weight of the specimens was measured every two, six, 12 and 24 h on the first day, and every 24 h thereafter on the second day, until five days had been completed. The water uptake was then calculated as a percentage.

3. Result and discussions

3.1. Polymorph and crystallinity analysis
The analysis of crystallography using XRD was performed to confirm the polymorph and crystallinity of MMCC and CNW-II on cellulose II. Both the MMCC and CNW-II diffraction patterns are shown in figure 1. It was found that MMCC shows the pattern of cellulose II by displaying two peaks located at $2\theta = 20.19^\circ$ and $21.93^\circ$, respectively, corresponding to the planes (110) and (020). After acid hydrolysis to produce nanoswhiskers, the CNW-II cellulose II pattern shows a wide peak at $2\theta = 20.23^\circ$ and $22.25^\circ$, indicating a lower crystallinity [30]. The hydrolysis process appears to have a significant impact on nanowhiskers. As many studies have reported, cellulose II is more easily hydrolysed than cellulose I [31, 32]. Since alkaline treatment (during the mercerisation of MCC) is known to cause swollen and loosen effects on fibril packaging, it promotes acid sensitivity during hydrolysis. The acid can be easily penetrated into the mercerised MCC, so it not only attacks the amorphous area, but also the crystalline sections. This can be clearly seen from the reduction in CI from 79.5% for MMCC to 55.3% for CNW-II (table 1). It is important to know that crystallinity is a crucial factor in influencing the properties of fibre, particularly in terms of chemical, mechanical and thermal properties, which will ultimately affect the properties of the composite made from it [1, 33].

3.2. Morphological and dimensional analysis
The morphology and dimensional analysis of CNW-II was determined using TEM and the image is shown in figure 2.

The MMCC image is also displayed to provide more insight into the CNW-II analysis. The swollen condition of the MMCC shows the loose packing of its fibrils, which enables deep acid penetration during hydrolysis. The comparison of MCCs before and after mercerisation was conducted in our previous study [28]. As discussed earlier, acid appears not only to attack the amorphous region, but also to affect the crystalline...
segment of cellulose. The micrograph image of CNW-II shows that the swelling effect has occurred until the level of microfibril. In contrast to the native CNW (cellulose I polymorph nanowhiskers) typical of needle/rod shape, CNW-II displays granule-like shapes. The CNW-II dimension was found to be of an average length of 74.04 nm with a width of 21.36 nm. The length and diameter (l/d) ratio of CNW-II is 3.70 which is far smaller than that of the native CNW, which is usually more than 10 \[10\]. The shorter CNW-II size was also observed by other researchers which range around 10–40 nm as compared to CNW-I with range of 100–300 nm \[1, 2, 34, 35\]. This is attributed to the swelling of the crystalline region as the NaOH hydroxide ion penetrates during mercerisation. As it swells, it causes a shorter length and an increase in the diameter.

3.3. FTIR spectra analysis of nanocomposites film

The nature and structure of the fibre-matrix interface plays an important role in the physico-chemical properties of the composites. The chemical structures of all films were analysed using the FTIR spectroscopy and the spectra shown in figure 3. The spectra of all films show a typical pattern of polyurethane. As shown in figure 3(a), all JOPU/CNW-II films showed almost a similar pattern of neat JOPU spectra, except for peaks between 1600 and 1800 cm\(^{-1}\) (figure 3(b)), which will be explained later.

It is crucial to observe the existence of a peak made from unreacted isocyanate which is normally found at 2271 cm\(^{-1}\) for polyurethane synthesis \[36\].

No peak was found at 2271 cm\(^{-1}\), indicating that all films have been fully interconnected and free of unreacted isocyanate. At 3329 cm\(^{-1}\), the low peak was observed, attributing by –NH bond stretching vibration.

Figure 2. Micrograph (a) SEM of MMCC and (b) TEM of CNW-II.
The hydrogen bonds in JOPU’s composite films are also depicted. The other peak associated with –NH bond (in plane bending) was also observed at 1535 cm$^{-1}$. The visible peak of the C–O ether bond (stretching vibration) is 1223 cm$^{-1}$. All films also featured bands of 2850 cm$^{-1}$ (asymmetric stretching) characteristic of the –CH2-group. In addition, the signal attributable to the –CH3 group is 2918 cm$^{-1}$ [36, 37].

C–H stretching and C–N bonding showed peaks at 2918 and 1306 cm$^{-1}$, respectively. Intense peaks between 1800 and 1600 cm$^{-1}$ were observed in JOPU/CNW films (figure 3(b)). The peaks indicate the C=O stretching band of carbonyl urea groups [38, 39]. To explain this, urea is known to have been formed by the reaction of isocyanate to hydroxyl groups. In this study, 4, 4’-diphenyl-methane diisocyanate (MDI) was used and MDI is a type of aromatic isocyanate that is more reactive than aliphatic isocyanate, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI) [40]. Since MDI is very reactive, it is very sensitive to moisture by producing urea as a derivative once it reacts with moisture (water) [41]. The presence of hydroxyl in fibre has therefore increased the formation of urea in JOPU/CNW-II film. Hydroxyl groups may contribute to the cellulose chain itself or/and to the moisture content of CNW-II. Although the formation of urea still occurs in very low CNW-II loadings. It is known that nano fibres have larger surface. This larger area also contributed to the exposure of the hydroxyl group from the cellulose chain itself. At the same time, it also increases the attraction of moisture and increases the formation of urea.

3.4. Density, optical translucency and surface morphology of nanocomposite film

The density of films made from JOPU and JOPU/CNW-II was found to be maintained, which is 1.05 g/cm$^3$. The incorporation of low CNW-II content (0.1–1.5 wt%) does not result in a significant change in film density. The majority of the density contributors are responsible for the JOPU matrix. The examination of the optical translucency and surface morphology of the films was carried out using the light microscope and the SEM, respectively. Figures 4(a)–(c) shows optical translucency images showing neat JOPU film and JOPU/CNW-II film with the lowest to highest CNW-II loading. The initial colour of the film originates from the colour of the Jatropha oil used to make the polyol, which appears in a golden-yellow colour. The golden-yellow colour contributed to the low residual level of gossypol and its oil derivatives, which vary depending on the climate and locality of the Jatropha planted [42].

The film made from neat JOPU is clearly translucent. Due to the nanometric size and the good dispersion in the PU, the translucency of the films is barely disturbed [43]. In contrast, the translucency of the JOPU/CNW-II films has decreased after insertion of CNW-II even at the lowest loading. As loading increases, not only translucent, the colour was also affected. The darker golden orange was observed to be more CNW-II in the films. Although though translucent and colour were affected, each film appears to remain homogeneity, suggesting that the CNW-II was well distributed in the matrix. In addition, as mentioned in the preceding section, urea formation occurs parallel to the CNW-II loading content. The lack of translucent and colour can also be compounded by the urea trapped in the films.

![Figure 3. FTIR spectra of (a) JOPU and JOPU–CNW-II; (b) enlarges spectra 1600–1800 cm$^{-1}$](image)
3.5. Thermo-mechanical analysis

Thermogravimetric analysis (TGA) was used in composite products to quantify the polymer mass change that was subject to thermal change that was associated with transition or degradation properties. Optimising the process is essential for obtaining high-performance products which are stable and free from undesirable by-products. Figure 5 shows the thermogravimetric analysis of CNW-II, JOPU and JOPU/CNW-II films (TG and DTG curves). CNW-II demonstrated two-step pyrolysis in which the first step of pyrolysis corresponded to the evaporation of moisture. This indicated that the CNW-II contained a relatively high amount of moisture that was subsequently reacted to isocyanate during the production of JOPU/CNW-II films. As discussed earlier, this urea was trapped in the matrix and affected the properties of the films.

The neat JOPU film was the most thermally stable in contrast to the other films. For JOPU/CNW-II films, the TG and DTG curves appeared to be almost identical with a slight difference in thermal stability compared to the neat JOPU. Similar observations have been reported that thermal stability of PU composites has not been affected by the addition of cellulose nanowhiskers [44]. The TG curves indicated that the degradation of all films started at about 190 to 200 °C and ended at around 480 to 490 °C. DTG curves have generally shown that all films have a two-step degradation process that is identical to the plant oil-based polyurethane degradation pattern. As a whole, the first decomposition occurred at temperatures ranging from 320 to 330 °C and the second stage occurred at 425 to 450 °C.

This typical two-step degradation was due to the degradation of the hard (first degradation) and soft (second degradation) segments of the plant oil-based polyurethane polymer. In the first stage of degradation, urethane bonding began to decompose, followed by isocyanate and alcohol dissociation, followed by the formation of primary amines, oleins, secondary amines, and carbon dioxide [45]. Whereas, the degradation of the second stage was correlated with the dissociation of the polyol chain (soft segments) [46].

However, slight changes were observed following the incorporation of cellulose. JOPU/CNW-II has shown a trend that consistently has a slightly lower weight loss compared to JOPU. These attributes were the degradation behaviour of cellulose [47]. The properties of CNW-II itself are not thermally stable and have degraded as early as 176 °C. This also applies to the low crystallinity index of CNW-II, as discussed above. However, given that the content of CNW-II is relatively small, the overall trend of composite films has remained strongly influenced by the behaviour of JOPU. However, a slight increase in thermal stability was observed among JOPU/CNW-II films themselves, which can be attributed to the formation of a confined structure in the nanowhiskers cellulose and matrix [48].

3.6. Mechanical properties

Mechanical performance of all films as shown in table 2. Insertion of CNW-II gave a positive trend in tensile strength and Young’s modulus. Approximately 4-fold increase in strength (1.60 MPa) compared to neat JOPU (0.41 MPa). The Young Modulus also shows remarkable improvements. This improvement has been attributed to strong interactions between reinforced fibres and matrix and promotes stronger interfacial bonding [49]. Since cellulose II is more reactive than cellulose I, the formation of hydrogen bonding is expected to be higher. These strong interactions restricted the motion of the matrix during the tensile deformation, resulting in a stronger film [50, 51]. Stronger
films capable of maintaining a higher load, but a lower elongation at break was expected. The films became more fragile with the appearances of the CNW-II. This was due to the CNW-II rigidity that prevented the polymer segment and formed a separation of the microphase between the CNW-II and the matrix [52]. The mechanical characteristics of the material will depend on the relative volume fractions of the soft and hard phases and the intrinsic characteristics of each stage. These depend, in turn, on the details of the molecular packaging of the constituents, including the hydrogen bond density in the phases [53, 54]. High degree of intermolecular interaction and the presence of physical crosslinks between JOPU and CNW-II restrict the stability and flexibility of the chain. Without the presence of a chain extender, cellulose acts as a multifunctional cross-linking agent which reduces the mobility of the polymer. Nevertheless, higher Young's modulus values focus on providing evidence that composite films with higher CNW-II content are better at stress-strain ratio.

Table 2. Mechanical performance of JOPU and JOPU/CNW composite films.

| Film Types    | Young’s Modulus (MPa) | Tensile Strength (MPa) | Elongation at Break(%) |
|---------------|-----------------------|------------------------|------------------------|
| JOPU          | 1.31 (±0.10)          | 0.41 (±0.04)           | 341 (±5.92)            |
| JOPU/CNW-II 0.10 | 4.58 (±0.74)          | 0.82 (±0.08)           | 172 (±2.66)            |
| JOPU/CNW-II 0.25 | 6.64 (±0.68)          | 0.90 (±0.06)           | 149 (±1.64)            |
| JOPU/CNW-II 0.50 | 18.86 (±1.03)         | 1.02 (±0.09)           | 80 (±1.16)             |
| JOPU/CNW-II 1.00 | 23.41 (±1.63)         | 1.65 (±0.06)           | 64 (±2.30)             |
| JOPU/CNW-II 1.50 | 29.24 (±2.31)         | 1.60 (±0.02)           | 69 (±0.99)             |

Figure 5. Thermogravimetric analysis of JOPU and its composite films.
3.7. Water uptake
The water absorption profile of the JOPU and JOPU/CNW-II films is shown in figure 6. All composite films have seen an increase in water adsorption along with an increase in the CNW-II content. This was expected due to the hygroscopicity of cellulose with the addition of cellulose II polymorph reactivity, all JOPU/CNW-II films show about 6% additional water absorption when 0.1% of CHW-II was inserted. However, the additional CNW-II inserts from 0.1 wt% to 1.5 wt% show insignificant water uptake differences, with only about 3% difference (total 12% water uptake for 1.5 wt% CHW-II films). It may be due to the fact that some of the CNW-II was embedded in JOPU and therefore restricted the water from being absorbed. In fact, the presence of urea does not make a significant contribution to water absorption since urea is soluble in water.

4. Conclusions
As a result, CNW-II was successfully isolated showing granule-like whiskers. The scale was 74.04 nm in length and 21.36 nm in width. The CNW-II cellulose II polymorph was also confirmed by the XRD analysis and its crystallinity index was found to be small (55.3%) compared to the MMCC (79.5%). Based on the FTIR analysis, the spectra of all films display a typical polyurethane pattern. The JOPU spectra found dominant due to the very low CNW-II volume content of the composite film. No peak was observed at 2271 cm$^{-1}$, indicating that all films were completely interlinked and free from unreacted isocyanate. The density of all films was determined to be maintained at 1.05 g cm$^{-3}$. Slight changes in film colour and translucent as well as darker film colour are incorporated with 1.5% of CNW-II. The same pattern was observed for surface morphology JOPU/CNW II 1.50, indicating rough surface characteristics. Thermal degradation curves appeared to be almost identical to the minor difference in thermal stability for all composite films. The most thermally stable of all films was found by the neat JOPU. Mechanical properties (with the exception of elongation at break) show an enormous increase with the addition of CNW-II in JOPU film. The elongation at break was gradually reduced however as the CNW content in the JOPU matrix increased. The increase in CNW-II also increase the water absorption performance as expected.

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ORCID iDs
S O A SaifulAzry @ https://orcid.org/0000-0003-1093-0968
M M Aung @ https://orcid.org/0000-0002-6613-0700
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