



Article Physico-Mechanical Study of CMC/BFO/PoPD Nanocomposite Films Reinforced with Cellulose Nanocrystals (CNC_{MCC}) for Effective Photocatalytic Removal of Methyl Orange

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Abstract:** The present study was conducted to develop a nanocomposite film of carboxymethyl cellulose (CMC) reinforced with cellulose nanocrystals isolated from microcrystalline cellulose (CNC_{MCC}) in the presence of bismuth ferrite (BFO)/poly-o-phenylenediamine (PoPD). The physicochemical properties, the mechanical and thermal stability, and its photocatalytic activity towards the removal of methyl orange (MO) were determined. Results show that the integration of CNC_{MCC} into the CMC matrix enhanced the mechanical strength of the film. The tensile strength (TS) of the nanocomposite film increased from 0.205 to 0.244 MPa, while elongation at break (EB) decreased from 201.44 to 168.78% in the presence of 20 wt.% of CNC_{MCC}. The incorporation of CNC_{MCC} in the CMC matrix substantially enhanced the nanocomposite's thermal stability from 181.16 to 185.59 °C and decreased the degradation residue from 72.64 to 63.16%. The determination of the photocatalytic activity of the CMC/CNC_{MCC}/BFO/PoPD composite film revealed the removal of methyl orange (MO) of 93.64% with high structural integrity after 3 h of treatment. Thus, the isolated CNC_{MCC}-reinforced CMC/BFO/PoPD composite film can be used as a photocatalyst for the removal of organic pollutants from wastewater, including the methyl orange.

Keywords: nanocomposite; physicochemical; photocatalytic activity; cellulose nanocrystal (CNCs); microcrystalline cellulose; mechanical strength; methyl orange

1. Introduction

Creating synergies between the various phase constituents for smart materials and meeting the expected design expectations became a significant focus in recent years. Complementary to this intention, the nanocomposite polymer materials with high performance and excellent mechanical and thermal stability have received potential attention, because their constituent materials have better properties than their materials [1]. A study reported that the combination of different forms of semiconductors improves the properties of nanocomposites. The TiO_2 possesses a bandgap of 3.0–3.2 eV. It has been widely applied for its functionality on photodegradation with strong light absorption in the UV region. Although its photocatalytic activity has been extensively reported, the material's wide band gap energy restricts it from being used in the visible light spectrum. As a result, several attempts to enhance the photocatalytic and light harvesting functions of the semiconductor rare compelling. Functionalized membranes/nanocomposite films can bind specific pollutants and catalyze degradation reactions by incorporating various semiconductor nanoparticles embedded into the matrices. Numerous studies have attempted to integrate

TiO₂ with other adsorbents, such as polymers to develop a membrane or nanocomposite film with improved properties. For instance, polypyrrole (PPy)-TiO₂, TiO₂-rGO (reduced graphene oxide), and poly (vinyl alcohol)/titanium dioxide (PVA/TiO₂) nanocomposites [2–4] have been designed for the enhancement of photocatalytic reactions towards the removal of water contaminants.

In recent years, surface water pollution with azo dyes from various industrial effluents poses severe environmental pollution and a human health concern. Methyl orange (MO) is an anionic azo dye. It is carcinogenic, bio-persistent, mutagenic, and toxic to aquatic lives and human health [5–7]. The MO is stable in water and shows low biodegradability [6]. It is soluble in water, and therefore it is difficult to remove the methyl orange from wastewater using common wastewater treatment processes [5-7]. Bismuth ferrite, BiFeO₃ or (BFO), is a multiferroic substance that exhibits both weak ferromagnetism and high ferroelectricity at room temperature [8]. In contrast to TiO_2 , BFO has a narrow band gap of 2.2 eV, and it facilitates a photocatalysis reaction under both visible and direct sunlight. Nevertheless, the recorded photocatalytic activity and efficiency of BFO for degradation of anionic organic dyes such as methyl orange (MO) was very low due to the disadvantages of poor carrier mobility and the rapid recombination of photogenerated electron-hole pairs [9,10]. The BFO has been doped or combined with other conductive polymers such as poly-o-phenylenediamine (PoPD), poly-pyrrole (PPr), and polyaniline to enhance its photocatalytic activity (PANi). The combination of BFO and conductive polymers would provide a synergistic effect and reduce the recombination rate of photogenerated electron-hole pairs [11].

Poly-o-phenylenediamine, PoPD, is a conducting polymer made up of repeating units of 2,3-diaminophenazine or quinoraline. PoPD is synthesized by replacing the hydrogen atom with an amino group in the oPD monomer, which is an aniline derivative. This polymer possesses a wide conductivity range, high electroactivity, excellent optical and magnetic activity, and superior heat and environmental stability [11]. The chemical and electrochemical methods are both viable choices of synthesizing PoPD [12]. The combination of semiconductors and conductive polymers with an extended π -conjugated electron structure could boost the photocatalytic performance of the composite within the visible light range [11]. Nonetheless, incorporating BFO and PoPD without any supporting material resulted in unstable aggregation and significantly reduced the specific surface area and photocatalytic activity [13]. The supporting material is known to improve the dispersion stability effectively and increase the reusability of the nanocomposite.

Carboxymethyl cellulose (CMC) is a polysaccharide derivative from cellulose which is soluble in water because of its hydrophilic properties in nature. CMC is a biodegradable polymer and a low-cost-to-produce material that is non-toxic to the environment; it is semicrystalline and has outstanding film-forming performance but appears to demonstrate low conductivity [14]. Cellulose is the most widely used polymer, and it is used in a wide range of applications, including water treatment. Most researchers attempted to develop a technique of water treatment using biodegradable polymers including CMC by integrating carbohydrates, proteins, lipids, and other functional materials to improve the photocatalytic nature of thin films [15]. Some studies have been using CMC as biopolymers due to the nature of CMC properties in nanocomposite films' preparation. The CMC polymer has a wide application in cosmetics and food as a water-resistant agent and dispersing stabilizer. This polymer's backbone structure contains various functional groups, such as carboxylic and hydroxyl groups, enhancing its hydrophilicity in nature, and significant for an adsorption property towards water contaminants. As a result, CMC can be used in various applications, including the adsorption of contaminants including heavy metals and dyes [16].

Biopolymer films, despite their advantages, suffer from poor mechanical properties. Numerous studies have been conducted to improve the mechanical properties of biopolymer-based films by incorporating hydrophobic materials, inorganic materials, and other polymers or small molecules [16]. According to the findings of Zahedi and co-workers [17], inserting MMT or TiO₂ nanoparticles (NPs) into the polymer matrix improved the mechanical properties of nanocomposite films. Their finding demonstrated the CMC-Na-MMT-TiO₂ nanocomposites showed advanced performance and enhanced mechanical strength of nanocomposite films. The inclusion of two or more types of nano-sized filler manifolds has improved films' properties when compared to films containing only one type of NP [17]. The physical properties of CMC/ChNW (chitin nanowhiskers)/ZnO-Ag nanocomposites films were successfully investigated by Oun and Rhim [18]. They demonstrated that adding ZnO-Ag NPs improved the thermal stability, mechanical power, and contact angle of a CMC/ChNW composite film, and that they increased even further with the addition of Ag NPs [18]. In another study, Mohammadi et al. [19] determined the physico-mechanical properties of fabricated CMC/okra mucilage (OM)/ZnO composite films. They demonstrated that integrating ZnO NPs into CMC/okra mucilage film improved the film's tensile strength (TS) and increased water solubility (WS) of the film. The enhancement of the film properties is related to the network of random coil polysaccharides of galactose, rhamnose, and galacturonic acid available from okra mucilage [19]. The CMC-based films reinforced with CNCs exhibited a substantial improvement in the mechanical strength and water vapor barrier of the composite films, according to an observation based on the analysis by Oun and Rhim [20]. CNCs derived from the ammonium persulfate (APS) oxidation method have an excellent ability to be used as a reinforcing filler in biopolymer-based films, which applies in food packaging films, nanopapers, hydrogels, and biomedical applications [20].

The goal of the BFO/PoPD/CMC nanocomposite films reported in this work was to improve photocatalytic efficiency by immobilizing bismuth ferrite (BFO) and poly-ophenylenediamine (PoPD) in the presence of CMC hydrogel. Furthermore, the incorporation of cellulose nanocrystals (CNCs) isolated from microcrystalline cellulose (MCC) using an ammonium persulfate (APS) technique within CMC/BFO/PoPD nanocomposite films for mechanical and physicochemical properties enhancement was conducted. To the best of our knowledge, there is no study that has yet to be conducted on the incorporation of PoPD polymer and BFO nanoparticles into the CMC matrices in the presence of CNC_{MCC} inclusion for the practical function in water treatment and purification.

2. Materials and Methods

2.1. Chemicals and Materials

Bismuth nitrate pentahydrate (98% purity), Iron (III) nitrate nanohydrate (98% purity), Carboxymethyl cellulose sodium salt (low viscosity), Ammonium persulfate (98% purity), and monomer o-phenylenediamine (oPD) (99.5% purity) were purchased from Sigma-Aldrich, Kuala Lumpur, Malaysia. (Sigma-Aldrich), Microcrystalline cellulose, Citric acid, and methyl orange dyes were obtained from HmbG chemicals, Kuala Lumpur, Malaysia.

2.2. Synthesis of Bismuth Ferrite Nanoparticles

Bismuth ferrite was synthesized following the method reported by Satar et al. [21]. Bismuth nitrate pentahydrate (3.0 mmol) and iron nitrate nonahydrate (0.5 mmol) were weighed accurately and dissolved in 25 mL of distilled water to form a 0.2 M precursor solution. Then, 10 mL of BFO solution was added into 40 mL of carrageenan solution (0.5 wt.%) with vigorous stirring. The mixture was heated at 80 °C for 2 h to form a precursor with a pale yellow color. The precursor solution's pH was adjusted to pH 10 by adding 0.1 M of sodium hydroxide, and the color of the precursor solution changed to dark brown. The mixtures were dried overnight in the oven at a temperature of 80 °C. The dried brown powders were then transferred to a crucible and calcined in a muffle furnace for 2 h at 550 °C. The BFO powder was kept in the small vial before being further used.

2.3. Synthesis of Poly-o-Phenylenediamine (PoPD) via Chemical Polymerization Method

Poly-o-phenylenediamine (PoPD) was synthesized using a previously described method of Li et al. [22]. Monomer o-phenylenediamine (oPD) (5 mmol) and APS (15 mmol)

were weighed accurately and dissolved in 25 mL of double distilled water at room temperature. Under vigorous stirring, both solutions were mixed and left at room temperature for 24 h. After 24 h, a dark brown precipitate appeared, and the mixture was filtered and washed several times with distilled water and ethanol until the filtrate became colorless. Finally, the product was dried in the oven at 50 °C for 24 h. The PoPD powder was kept in a small vial before further use.

2.4. Synthesis of CMC/BFO/PoPD Nanocomposite Films

The citric acid (5.0 g) and carboxymethyl cellulose (CMC) powder (1.25 g) were weighed accurately and dissolved in distilled water. The amount of bismuth ferrite powder (3 wt.%) was weighed accurately and added into the solution gel after the CMC was completely dissolved. Poly-o-phenylenediamine (PoPD) (1 wt.%) was transferred to the gel solution, and the mixture was stirred until the material was completely dissolved. After that, the solution gel was poured into the petri dish and dried in the oven at 40 °C for 72 h.

2.5. Synthesis of CMC/BFO/PoPD Nanocomposite Film Reinforced with CNC_{MCC}

CNCs utilized as a reinforcing matrix were isolated from the microcrystalline cellulose (MCC) using the ammonium persulfate method (APS) as an oxidizing agent [20]. MCC was added to 50 mL of 1 M APS under vigorous agitation at 75 °C for 16 h. The suspension of CNCs was then centrifuged at 4000 rpm for 20 min and washed with distilled water until the pH reached to pH 4. Then, the pH was adjusted until pH 8 by using 1 M of NaOH. The suspension was then dried in the oven and was kept in the small vial before further use [20]. Certain amounts of cellulose nanocrystal (CNCs) (20% wt based on CMC's weight) were weighed accurately and dissolved into 19 mL distilled water. The mixture was stirred for 2 h until the CNCs were completely dissolved. Then, 5.0 g of citric acid was added, followed by adding 1.25 g of CMC powder. The mixture was stirred until the CMC powder is dissolved. Then, BFO powder and PoPD powder were added into the mixture in a 3:1 ratio. The mixture was then poured into the petri dish and dried in the oven at 40 °C for 72 h.

2.6. Characterization of Nanocomposite Films

Attenuated Total Reflectance—Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to analyze the functional group's presence in the BFO, PoPD, and the nanocomposite films using Perkin Elmer, FT-NIR Spectrometer Frontier Universal ATR sampling accessories. The scanning range is 600–4000 cm⁻¹, and the resolution is 8 cm⁻¹. The X-ray diffraction analysis was conducted to confirm the structural properties of prepared samples. The films were analyzed in the 2 θ range of 20°–70° with a PANalytical X'Pert PRO θ –2 θ equipped with graphite monochromatic Cu K α radiation (λ = 1.5406 Å) at a 40 kV operation. The surface morphology of nanocomposite films was analyzed using Scanning Electron Microscopy Energy Dispersed X-ray (SEM-EDX) FEI-QUANTA FEG 650. The sample was coated with gold before the characterization of thermal stability of the fabricated composites films was determined using thermogravimetric analyses with temperature ranges from 30 °C to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.6.1. Mechanical Properties

Mechanical properties in this work include tensile strength (TS), elongation at break (EB), and Young's modulus (YM). The test was conducted using an ASTM D822 machine. Firstly, the film samples were cut accurately into a strip of 0.06 m \times 0.013 m. The grip separation, length, speed, load, and extension range are 0.015 m, 0.03 m, 13 mm/min, 0–200 N, and 0–1000 mm, respectively.

2.6.2. Contact Angle

For the contact angle (CA) determination, the film samples first were cut into 0.02 m \times 0.02 m. The film samples were fixed on the horizontal stage, and 6 μL of

water was dropped on the film surface using a micro-syringe. The results started to be recorded after dropping the water. The CA analysis was conducted by using a CA analyzer.

2.6.3. Water Absorption Test

A water absorption test was conducted by cutting the films into $0.02 \text{ m} \times 0.02 \text{ m}$ and dried at 40 °C for 24 h until the film sample reached a constant weight. The dried film samples were then immersed in a covered beaker filled with 50 mL of distilled water at 25 °C for 24 h with periodical gentle manual agitation. The water absorption was calculated by using the formula in Equation (1).

$$Water \ Absorption(\%) = \frac{W_t - W_o}{W_o} \times 100 \tag{1}$$

where W_0 and W_t were the initial dry weight and weight of the sample after soaking, respectively.

2.6.4. Photocatalytic Activity

The photocatalytic activity was carried out under sunlight to assess the percentage removal of methyl orange dye and observed the film's stability after 3 h of treatment. The CMC/BFO/PoPD (without reinforced CNC_{MCC}) and $CMC/CNC_{MCC}/BFO/PoPD$ films (with varying 10–30 wt.% CNC_{MCC}) were suspended into the flask containing 50 mL of 10 ppm of methyl orange. The solution was shaken using a mechanical shaker at 200 rpm for 3 h under direct sunlight. The MO concentration was determined using a UV-vis spectrophotometer, at the wavelength of 200–800 nm. The percentage removal of methyl orange was calculated using Equation (2). C_o (mg/L) and C_t (mg/L) represent the initial and the final concentrations of MO after 3 h of treatment, respectively.

$$\text{Removal}(\%) = \frac{C_o - C_t}{C_o} \times 100 \tag{2}$$

3. Results

3.1. Fabrication of CMC/BFO/PoPD Reinforced with CNC_{MCC}

As previously mentioned, CMC/BFO/PoPD reinforced with cellulose nanocrystal (CNC_{MCC}) was successfully prepared. CNC_{MCC} were integrated into the transparent membrane of CMC matrices, which resulted in high mechanical stability. The physicochemical properties of CMC/BFO/PoPD reinforced with CNC_{MCC} were investigated, as well as the evaluation on the photocatalytic performance towards methyl orange, MO.

3.2. Characterization of Materials

3.2.1. XRD and FTIR Analysis of CMC/BFO/PoPD Reinforced with CNC_{MCC} Composites

The phase structure of studied composites has been determined by X-ray diffraction patterns, as shown in Figure 1. CNC_{MCC} exhibits diffraction peaks at $2\theta = 22.5^{\circ}$ indexed for (002), corresponding to the characteristic diffraction pattern of the cellulose I structure. The diffraction peaks of BFO appear at 22.58°, 32.18°, 39.64°, 46.31°, 52.06°, 57.33°, and 67.48° indexed to the diffraction planes of 012, 110, 202, 024, 116, 300, and 220. Peak 110 appeared to be the significant peak for BFO, and it revealed that the calcined powder of BFO has high crystallinity without forming any secondary phases in the diffractogram. Due to the amorphous properties of PoPD, there is no significant peak observed from the PoPD diffractogram. Two diffraction peaks of CMC appeared at $2\theta = 23.32^{\circ}$ and 26.07°, indicating its semi-crystalline structure in nature. However, the CMC's amorphous phase can be seen after introducing BFO and PoPD towards the polymer film, as the crystalline diffraction peak of CMC becomes less intense [11]. The inclusion of CNC_{MCC} inside the system leads the film to be an amorphous phase. The appearance of a broad absorption band at 3428 $\rm cm^{-1}$ on ATR-FTIR spectrums of CMC/BFO/PoPD composite film and CMC/CNC_{MCC}/BFO/PoPD composite film correspond to O-H stretching, which is primarily due to the peak of CMC (Figure 2). The absorption band was around 2900 cm^{-1}

due to $-CH_2$ stretching, while the intense peak between 1706 and 1720 cm⁻¹ belonged to the C=O stretching of the polymer. The absorption band was around 1390 cm⁻¹, 1330 cm⁻¹, and 1060 cm⁻¹ due to C-H bending, O-H bending, and C-O-C stretching, respectively [11]. The -NH₂ peak, which corresponds to PoPD, may be overlapped with the -OH stretching peak around 3500 cm⁻¹. The peak is probably in negligible absorption due to the low concentration of PoPD within the system. Further characterization to confirm the presence of BFO and PoPD within a system was later conducted.

3.2.2. Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) of CMC film, CMC/CNC_{MCC} film, CMC/BFO/ PoPD composite film, and CMC/CNC_{MCC}/BFO/PoPD composite film is shown in Supplementary Figure S1, and the results obtained are summarized in Table 1. The derivative thermogravimetric (DTG) curve of CMC revealed a three-step decomposition, with the first weight loss beginning at an onset temperature of 160.01 °C and linked to the loss of structurally bound water. The hydroxyl group decomposition resulted in a 65.30% weight loss and a 34.70% percent residue (approximately 1.837 mg) in the first decomposition. As depicted in Figure S1a, further heating of the sample resulted in another two subsequent decomposition phases at 225.5 °C and 510.0 °C, with the removal of 18.95% and 0.741%, respectively.



Figure 1. XRD diffractogram of (a) CNCs powder, (b) BFO powder, (c) PoPD powder, CMC film, CMC/BFO, CMC/BFO/PoPD, and CMC/CNC_{MCC}/BFO/PoPD.



Figure 2. ATR-FTIR spectrum of (**a**) CMC, (**b**) CMC/CNC_{MCC}, (**c**) CMC/BFO/PoPD, and (**d**) CMC/CNC_{MCC}/BFO/PoPD composite film.

Table 1. Thermogravimetric analysis of CMC film, CMC/CNC_{MCC} film, CMC/BFO/PoPD composite film, and $CMC/CNC_{MCC}/BFO/PoPD$ composite film.

Sample	Decomposition Temperature (°C) T _{onset} /T _{end}	Char Residue (%)
СМС	157.60/305.00	34.70
CMC/CNC _{MCC}	187.07/310.30	33.28
CMC/BFO/PoPD	181.16/287.07	16.02
CMC/CNC _{MCC} /BFO/PoPD	185.59/311.26	12.57

From the inspection of the DTG curve of CMC/CNC_{MCC}, three decomposition steps are observed in which the first weight loss profile takes place at an onset temperature of 187.07 °C and is most probably attributed to the loss of moisture on the sample; 33.28% (3.16 mg) of residue is left. Consequently, with further heating of the sample at 310.30 °C and 742.37 °C, only 15.07% and 13.98% of the left residue are respectively obtained. In the case of CMC/BFO/PoPD composite film, three decomposition steps were observed at a temperature 181.16 °C in which the first weight loss is due to the loss of bound water (72.64% weight loss). Further heating resulted in another two-step decomposition of the composite at 287.07 °C (16.02% weight loss) and 756.58 °C (0.96% weight loss).

From the DTG curve of the CMC/CNC_{MCC}/BFO/PoPD composite film, it was found that three decomposition steps took place in which the first decomposition happened at an onset temperature 185.59 °C (2.65 mg residue) due to the loss of structurally bound water. Two more decomposition steps resulted from the additional heating process at 311.26 °C and 714.49 °C, with left residues of 12.57% and 11.09%. As can be seen in Table 1, the incorporation of CNC_{MCC} in the CMC matrix increases the thermal stability of the composite film by increasing the thermal decomposition temperature of the film. However, the increase in the thermal stability of the CNC_{MCC}-reinforced CMC/BFO/PoPD nanocomposite films attributes to the hydrogen bonds between the CNC_{MCC} and CMC polymer matrix, as well as the increase in the crystallinity of the composite film because of the crystallization of CNC_{MCC}. Similarly, Mandal and Chakrabarty [23] and Li et al. [24] reported that the increase in the thermal stability of the CMC-based composite film was due to the incorporation of the CNC in the CMC polymer matrix.

3.2.3. Scanning Electron Microscope (SEM)

Figure 3a,b demonstrates the morphologies of BFO and PoPD powder from SEM analysis, which clearly indicates that they are composed of a high amount of homogeneous distribution of rhombohedral and spherical particles. The SEM micrographs in Figure 3c,d

revealed that the surface of the CMC film and CMC/CNC_{MCC} film (control films) were smooth, continuous, and homogeneous, with no cracks or irregularities; this indicates that the CNC_{MCC} was evenly distributed within the CMC matrix without agglomeration. This might be attributed to compatibility between the CNC_{MCC} and CMC matrix because of their similar chemical structures [20,24]. Besides, the small dimensions of CNC_{MCC} might have played an effective role in the homogeneous distributions of CNC_{MCC} in the CMC matrix. The addition of BFO resulted in back-scattered electrons of metal particles on the film surface, indicating the presence of Bi and Fe distributed within the CMC matrix. Furthermore, it was observed that BFO and PoPD had an effect on the microstructure of the nanocomposites, and therefore the surface of the CMC/BFO/PoPD and CMC/CNC_{MCC}/BFO/PoPD composite films had a more heterogeneous and rough structure than the control films, as shown in Figure 3e,f. This can be attributed to the agglomeration of the filler with PoPD and BFO in the composite films. The presence of PoPD in the system can be observed and confirmed using SEM-EDX (Figure S2).



Figure 3. SEM images for (**a**) BFO powder, (**b**) PoPD powder, (**c**) CMC, (**d**) CMC/CNC_{MCC}, (**e**) CMC/BFO/PoPD, and (**f**) CMC/CNC_{MCC}/BFO/PoPD composite film.

3.2.4. Photocatalytic Activity

The photocatalytic activity of the CMC/BFO/PoPD (without CNC_{MCC} reinforced) and CMC/CNC_{MCC}/BFO/PoPD nanocomposite films with varying 10–30 wt.% of CNC_{MCC} for the degradation of 10 ppm methyl orange was carried out, as shown in Figure 4. Figure 4a,b depicts the UV-visible absorbance and percentage removal of methyl orange before treatment, control CMC/BFO/PoPD, and CMC/BFO/PoPD/CNC_{MCC} composite films after 3 h of treatment. It was found that the percentage removal of MO was obtained at about 87% using the CMC/BFO/PoPD (without CNC_{MCC} reinforced). However, the percentage MO removal increased with an increasing percentage of CNC_{MCC} incorporation to the CMC matrix from 10 wt.% to 20 wt.% and decreased thereafter. The highest MO removal of about 94% was obtained using 20 wt.% of the CNC_{MCC} incorporation to the CMC matrix. The increase in the MO removal with the incorporation of the CNC_{MCC} incorporation to the CMC matrix attributes to the increase in the active functional group on the surface of the CNC-reinforced CMC/BFO/PoPD composite film, which substantially enhanced the affinity towards the MO and therefore increased the removal efficiency [25]. Figure 4c shows the photographic image of the CMC/BFO/PoPD composite film before and after treatment. It was found that the CMC/BFO/PoPD composite film after treatment was ruptured and broken after 3 h of photocatalytic absorption of MO from the aqueous solution. This can be attributed to the relatively weak mechanical strength of the CMC/BFO/PoPD composite film without reinforcement of the CNC_{MCC}. However, the incorporation of CNC_{MCC} in the CMC matrix increased the mechanical strength and integrity of the CMC/CNC_{MCC}/BFO/PoPD composite film. Therefore, it was able stand with shear forces generated during the photocatalytic adsorption. This can be attributed to the CMC/CNC_{MCC}/BFO/PoPD composite film without an intact and ruptured surface after the photocatalytic absorption of MO (Figure 4d).

3.2.5. Mechanical Properties

Table 2 shows the effect of incorporating CNC_{MCC} into the system on the mechanical properties of the composite film. Based on the observations, the CMC control film initially has a tensile strength (TS) value of 0.121 MPa. The addition of CNC_{MCC} to the CMC matrix improved the film's tensile properties. CNC_{MCC} increased the tensile strength of the CNC_{MCC}/CMC film to 0.259 MPa. Further investigation into the ternary system revealed that the incorporation of CNC_{MCC} into the CMC/BFO/PoPD nanocomposite film increased from 0.205 MPa to 0.244 MPa. The enhanced mechanical properties of nanocomposite films were most likely caused by the strong interfacial interaction between CNC_{MCC} and the CMC polymer matrix, which was directed by a large amount of hydrogen bonding between hydroxyl (-OH) and carboxyl groups (-COOH) on the surface of CNC_{MCC} after APS treatment [24]. The band was observed at 3429 cm^{-1} in the CMC spectrum where the (-OH) group was shifted to lower frequencies 3367 cm⁻¹ in the CMC/CNC_{MCC} spectrum. However, the tensile strength of the CMC/CNC_{MCC}/BFO/PoPD composite film was lower than the CMC/CNC_{MCC}. This might be due to the agglomeration of the CNC_{MCC} with PoPD and BFO in the composite films, which can be attributed to the heterogeneous and rough surface structure of the CMC/CNC_{MCC}/BFO/PoPD composite film (Figure 3f). The elongation at break, EB, of a CMC/BFO/PoPD nanocomposite film reinforced with CNC_{MCC} reduced from 100.72 to 84.389 percent. The high content of CNC_{MCC} within the CMC matrix restricted matrix chain movement, resulting in the agglomeration of CNC_{MCC} within the system. As a result, the film becomes more rigid, leading to a decrease in the elongation at break values. Similarly, Hanid et al. [26] observed that the elongation at break values decreased with increasing the halloysite nanofiller in the polymer matrix due to increasing the rigidity of the nanocomposites. The relationship between tensile strength (TS) and Young Modulus (YM) of the studied films showed that an increase in the TS resulted in increasing Young Modulus (YM). The YM of a CMC film reinforced with CNC_{MCC} has been increased from 0.0008 to 0.0017 MPa. This is due to the interaction of



the CNC_{MCC} with the polymer matrix, which prevented the polymer chain's molecular orientation, thereby increasing the modulus [26].

Figure 4. (a) UV-visible absorbance and (b) percentage removal of methyl orange of different percentages of CNC_{MCC} added to CMC/BFO/PoPD film. The photographic images of the nanocomposite films (c) CMC/BFO/PoPD and (d) CMC/CNC_{MCC}/BFO/PoPD before and after 3 h of photocatalytic activity for the removal of methyl orange dye.

Film Samples	TS (MPa)	EB (%)	Young's Modulus (MPa)
СМС	0.121 ± 0.032	147.556 ± 20.21	$0.0008 \pm 1.14 imes 10^{-4}$
CMC/CNC _{MCC} (control)	0.259 ± 0.035	152.889 ± 17.20	$0.0017 \pm 6.53 \times 10^{-5}$
CMC/BFO/PoPD	0.205 ± 0.004	201.444 ± 11.69	$0.0010 \pm 7.84 imes 10^{-5}$
CMC/CNC _{MCC} /BFO/PoPD	0.244 ± 0.016	168.778 ± 15.00	$0.0014 \pm 4.91 imes 10^{-5}$

Table 2. Mechanical properties of the composite films in terms of tensile strength (TS), elongation at break (EB), and Young Modulus (YM).

Value is expressed as mean \pm standard deviation of three readings.

3.2.6. Contact Angle and Water Absorption Test

The contact angle (CA) was used to assess the hydrophilicity and hydrophobicity nature of the nanocomposite films. CMC and CMC/CNC_{MCC} were considered as hydrophilic films since the CA value is less than 65°. The addition of CNC_{MCC} to the CMC matrix decreased the hydrophilicity of the nanocomposite film, as shown in Table 2. This could be due to the strong hydrogen bond formed between the CNC_{MCC} and CMC matrix, which reduced the free -OH group in the system and thus reduced the film's contact with the water molecule. Figure 5 clearly shows the significant difference in the shape of the water angle between the CMC control film and the CMC/BFO/PoPD/CNC_{MCC} film. The analysis of water absorption is an important parameter for biopolymer films. The result of the water absorption analysis is also presented in Table 3. The percent water absorption of the control film CMC is found to be 13.129%. The addition of CNCs in the CMC matrix results in a significant increase in the water absorption of the film to 26.982%. The hydrophilicity structure of CMC and CMC/CNC_{MCC} molecules make the film matrix more accessible to water, resulting in rapid absorption by CMC and CMC/CNC_{MCC}. The water absorption of CMC/BFO/PoPD nanocomposites films reinforced with CNC_{MCC}, on the other hand, decreased significantly from 7.961% to 6.335%. The decrease in water absorption of the nanocomposite film as a function of BFO and PoPD indicated that the film sample had increased its cohesiveness. As can be seen in Table 3, there is a negative correlation between contact angle and water absorption. Generally, the contact angle of a composite film depends on the surface hydrophobicity and roughness. The higher the contact angle of a composite film, the higher the hydrophobicity and therefore the lower the percentage of water absorption [27]. It was found that the incorporation of CNC_{MCC} in the CMC/BFO/PoPD composite film increased the contact angle from 85.537° to 88.843°, but decreased the percentage water absorption from 7.961% to 6.335%. Thus, it can be concluded that the incorporation of the CNC_{MCC} in the CMC/BFO/PoPD composite film increased hydrophobicity, and therefore it had higher rigidity in photocatalytic absorption of MO dye from the aqueous solution.



Figure 5. Contact angle images for (a) CMC and (b) CMC/CNC_{MCC}/BFO/PoPD nanocomposite film.

Contact Angle (Degree)	Water Absorption (%)
34.009 ± 3.312 42 197 + 1 447	$\frac{13.129 \pm 1.573}{26.982 \pm 2.823}$
42.197 ± 1.447 85.537 ± 11.666 88.843 ± 19.941	$\begin{array}{c} 20.962 \pm 2.823 \\ 7.961 \pm 1.419 \\ 6.335 \pm 1.846 \end{array}$
	Contact Angle (Degree) 34.009 ± 3.312 42.197 ± 1.447 85.537 ± 11.666 88.843 ± 19.941

Table 3. Contact angle (CA), and water absorption of film samples.

Value is expressed as mean \pm standard deviation of three readings.

4. Conclusions

To summarize, the fabrication of the CMC/BFO/PoPD film was successfully synthesized. The incorporation of CNC_{MCC} nanofillers into the CMC matrix significantly improved the physicochemical properties, thermal stability, and photocatalytic properties of the nanocomposite films. The inclusion of 20 wt.% CNC_{MCC} increased the tensile strength (TS) and decreased the elongation at break (EB) of the CMC/BFO/PoPD nanocomposite films. The addition of CNC_{MCC} remarkably increased the photocatalytic activity and mechanical stability of the CMC/BFO/PoPD film after 3 h of treatment. The reinforcing filler of CNC from MCC have a high potential to be used in any photocatalyst-embedded biopolymer film to improve the physico-mechanical properties and enhanced photocatalytic activity, particularly for the degradation of water contaminants.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/jcs5060142/s1, Figure S1: Thermogravimetric analysis of (**a**) CMC, (**b**) CMC/CNC_{MCC}, (**c**) CMC/BFO/PoPD, and (**d**) CMC/CNC_{MCC}/BFO/PoPD composite film, Figure S2: The SEM-EDX of CMC/CNC_{MCC}/BFO/PoPD nanocomposite film.

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