Study of Cellulose Nanocrystals (CNC) & Polyvinyl Alcohol (PVA) Composite Film Modified using Silica and Polybutylene Terephthalate (PBT) as a Transparent, Hydrophobic, Self-Cleaning Cover

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Abstract

A green alternative to counteract solar panel soiling was studied using nanocellulose composites. Cellulose nanocrystals (CNC) synthesized from acid hydrolysis was blended with Polyvinyl alcohol (PVA), and Polybutylene terephthalate (PBT) and powdered Silica (SiO2) were used to modify its surface to produce a transparent, hydrophobic film. The objective was to test the composite film as a self-cleaning cover for solar panels. FTIR peaks of OH at 3284cm^{-1}, C-H at 2852 cm^{-1}, C=C at 1654 cm^{-1}, and C-O at 1087 cm^{-1}, and a 74.38% crystallinity index using X-ray Diffraction test confirmed the synthesis of CNC and presence of PVA. The OH peak's lower intensity in the composite film and dim peaks at 2918 cm^{-1} 2852 cm^{-1} confirmed PBT, and Silica's layering effect. The composite film exhibited an average transmittance of 92.18% of the incident light in the solar Photo-Voltaic working spectra (420nm-700nm). Results showed an average water contact angle (WCA) of 87.25°. When subjected to photocatalytic and hydrolytic decay, the film showed minimal changes in the FTIR plot, which confirmed its durability. The study proved the scope of CNC/PVA with PBT/SiO2 films as transparent, hydrophobic, durable self-cleaning covers against solar soiling but warranted further research to make suitable properties better.

Keywords: Cellulose and crystals (CNC), Polyvinyl alcohol (PVA), Thin-films, Self-cleaning, Solar panels, Transparent, Hydrophobic, Poly butylene terephthalate (PBT)

1. Introduction

Electricity generation from solar energy using photovoltaic (PV) panels has been a growing field of study in recent years as an eco-friendly, regenerative form of energy source. The current decade is set to improve solar power generation in cost and energy efficiency, making solar power affordable for application [1]. Solar power is harnessed using small modules of silicon p-n junction semi-conductor or PV cells, which trap solar radiation, generally in the wavelength range of 420 to 700nm [2]. The major problem associated with this energy conversion panels' blockage is soiling with dust and other particulate matter, bird dropping, and dew. It becomes a nuisance, especially in dust-prone cities, where PV cells are applied in street lightning, rendering timely maintenance problematic and expensive. In the Kathmandu valley, soiling induced transmittance losses up to 69.06% were observed with a power loss of 29.76% due to a dust deposition density of 9.6711 g/m^2 over a study period of several months in the dry season [3].

Cleaning robots are required for timely maintenance, especially in large solar farms. These mechanical robots are effective in areas with high soiling rates. In areas with limited access, sprinkler systems are used, while commercially available anti-soiling coatings are employed elsewhere [4,5]. Commercial coatings like fluorinated silanes are often used for anti-soiling purposes but have a disadvantage in durability, as they dissipate quickly on exposure to the atmosphere. So, hydrophobic coatings become expensive on the periodic application [6,7]. Some inorganic non-biodegradable coating such as TiO_2-Fe_2O_3 is economical enough but at the same time detrimental to the environment [8]. Therefore, a green alternative is needed for coating technology or alternatives to address this problematic area. Since the durability of coatings comes into question, eco-friendly superhydrophobic thin films were the key objectives of this research. Thin-films (<1mm) could be used as a protective cover layer for solar panels. The film's versatility could technically be used for applications where self-cleaning or *Lotus-effect* and dust repelling properties are required.

The contact angle (CA) value for hydrophobic pristine Polyethylene terephthalate (PET) is 75.3° ± 1.2° [9]. However, to become super hydrophobic, CA must be >120 °, which can be achieved by micro-and nano-corrugation either in the Cassie-Baxter (CB) state (which accounts for non-wettable water contact on the surface) and the Wenzel state (which accounts for wettable surface

contact). Ideally, for electronics, the CB state is preferred [10,11]. Low energy surface modifiers like silane or silica have been conventionally used to create the CB state and achieve either hydrophobicity or hydrophilicity [12, 13]. These modifiers also reduce the affinity of dust-water on the substrate [12]. If the film is to be used for solar panels, then the transmittance should be near 100%. So, a combination of self-cleaning, low dust water affinity, and near-perfect transparency is required for the thin film.

Recently, CNC has shown to be versatile with facile synthesis and variegated applications. Some of the standard synthesis techniques include thermo-mechanical and chemical treatments, which produce different properties based on source, technique, and starting cellulose concentration [14,15]. CNC is ideal for this application due to its convenient polymer making, accessibility, and eco-friendly nature, which is why it was employed to prepare hydrophobic films [16]. Polyvinyl alcohol (PVA) was used for its chemical resistance, optical properties, and bonding suitability with CNC [17], making it easier to modify its surface for hydrophobicity. Further, PVA's traditional cloudiness in water can be treated with methods such as hot-pressing or chemical treatments to improve its transparency to near-perfection [18]. Moreover, polybutylene terephthalate (PBT) and silica (SiO_2) coating on the surface added more hydrophobicity. The films prepared were characterized by Fourier transform Infrared spectroscopy (FTIR), X-ray diffractogram (XRD), CA, and ellipsometry to optimize its better performance [16,17,18,19].

2. Experimental

2.1 Materials

Microcrystalline cellulose (MCC) from Sigma Aldrich with 99 % purity (M_w=18000g/mol) with particle length ranging from 20µm to 100µm was used to nano fibrillate. Polymer matrix crystalline PVA from Nippon Gosei with a 98 % purity and PBT from Zhishang was purchased from Bandana Trade Concern (BTC) pvt ltd. Laboratory grade Toluene was used as a solvent for surface modification, and Silica gel-g from ACME synthetic chemicals with 99.8 % purity was also purchased from the BTC. 95 % by wt. of sulphuric acid (H_2SO_4) from Fisher Scientific and other necessary chemicals were used from the nanomaterial laboratory of Department of Applied Sciences, Institute of Engineering, Pulchowk Campus. In this work, all chemicals and materials were used without further modification and purification.

2.2 Preparation of CNC

CNC was prepared by acid-hydrolysis (64% by wt. H_2SO_4) of MCC [20]. The time of hydrolysis was vital to obtain the appropriate properties of the prepared CNC as longer hydrolysis time renders the breaking of coarse aggregates in the CNC's cellulose matrix leading to larger axial ratios, which is conducive to transparency [19,21].

50g of MCC was mixed with 50ml of de-ionized distill water and subjected to dropwise addition of 500ml of 64% by wt. H_2SO_4 for a hydrolysis time of 1h. The hydrolysis was carried out at a temperature maintained at 45℃ with a magnetic stirrer operating at 200-600 rpm, depending upon the mixture's viscosity [16,19]. The hydrolysis was interrupted by diluting the solution 10-folds by de-ionized distill water.

The solution was set to sit for 24h in a cool, dry environment. After the CNC suspension settled, the supernatant liquid was decanted off, and the sediment was kept for further purification. CNC at this time was highly acidic. The CNC suspension was centrifuged using a Virtuose PCF01 Lab Grade Centrifuge at 4000 rpm at room temperature (25°C) for 20 minutes while replacing de-ionized distill water at every batch until the pH was 6.53 (~7) measured using a Measuretech PHS-3C digital pH meter [16,19]. A 0.22µm Whatman membrane filter was used in a vacuum filtration process using a Joan VT335 vacuum filtration apparatus to remove any untreated MCC [22]. The filtrate obtained, characterized by opalescence in appearance, was determined to be the prepared CNC. The solution was kept in a 5℃ freezer for storage and for later use.

2.3 Preparation of PVA and CNC/PVA film

PVA was dissolved in de-ionized water (20g in 180ml) and heated at 60℃ for 5h for complete dissolution, using a magnetic stirrer at 800 rpm [23]. The PVA/CNC blend was created using a mixture of 80% PVA, 15% CNC suspension, and 5% Glycerol. CNC concentration was conducive to modify for hydrophobicity in the later process. Glycerol was added to improve the dispersion of CNC in the mixture. [17]. The mixture was kept at 60℃ and stirred for 30mins at 800 rpm.

The film of CNC/PVA blend was prepared by solution casting on a Boro-silicate circular glass plate of approximately 80 mm diameter. Another batch was spin-coated at 500 rpm onto the same type of glass plate. Both the solution cast and spin-coated glass were set to air-dry at 120℃ for 10mins in an oven, and for redundancy, one was left to dry overnight in a cool dry environment.

2.4 Surface Modification of CNC/PVA film with PBT/SiO_2

1g of silica-g with 2g of finely crushed Polybutylene terephthalate (PBT) was dissolved in 20ml of anhydrous Toluene. The suspension was ultra-sonicated for 10mins at 25℃. The resultant solution was kept in a glass petri dish, and the prepared films were dip-coated into it for 10mins on each side and left to dry in the ambient air under the assumption that PBT coats a thin layer of hydrophobic biodegradable plastic while silica enhances its hydrophobicity by surface modification [9].

2.5 Characterization

The film of CNC/PVA and the surface-modified film was analyzed for Fourier Transform Infrared (FTIR) spectroscopy using Perkin Elmer (FTIR2000) in attenuated total reflectance (ATR) mode within the wavenumber range of 4000 to 500 cm^{-1} [26] at the Central Department of Chemistry, Tribhuvan University (TU, Kritipur, Nepal). FTIR was also conducted for durability tests of CNC/PVA with PBT/SiO_2 after being exposed to photocatalytic and hydrolytic media.

The X-ray diffraction data were observed for CNC by using Bruker D2 Phaser Diffractometer at Nepal Academy of Science and Technology (NAST, Lalitpur, Nepal). The radiation used in the XRD was CuKα with a step of 0.02 and the powder sample was subjected to the diffraction from rotation of 10° to 80°. Samples used for XRD analysis were prepared by freeze-drying the suspension at -40°C of CNC via BIOBASE BK-FD10S Laboratory Freeze Drying Vacuum Freeze Dryer/Lyophilizer at Nano-Laboratory IOE, Pulchowk [28,29]. The crystallinity index was calculated using Segal's method [30] from equation (1) by obtaining the peak height of the crystalline region (I_{002}) and the amorphous region (I_{am}) [29].

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \qquad (1)$$

Spectroscopic ellipsometry was used to measure a change in light reflection when transmitted from the film using TF probe Armstrong tech Ellipsometer for a wavelength of 200 nm to 1100 nm. The test was carried out at the Department of Natural Sciences, Kathmandu University (Kavre, Nepal).

Contact angle (CA) was conducted at the Department of Natural Sciences, Kathmandu University using a contact-drop test apparatus Rame hart goniometer 200, tested with 4-6 µl of regular distilled water. The angles were observed from both ends.

3. Results and Discussion

3.1 Macroscopic features of the CNC/PVA film

The obtained CNC/PVA film resembled a plastic-like consistency. The film obtained from air dried (24h), spin coated on PET petri dish PVA/CNC film was qualitatively better. The film lacked any inconsistency in concentration unlike solution-casted films and were easy to peel off from the substrate unlike glass-substrate films. Fig. 1a and b are the macroscopic photographs of these films.

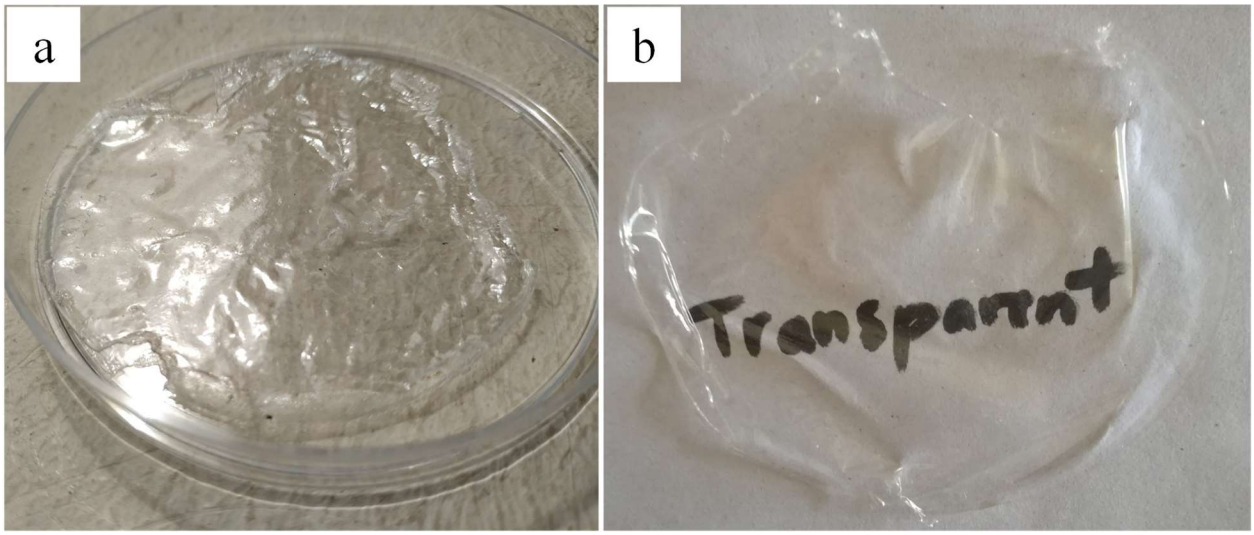


Figure 1. Prepared CNC/PVA film (a) before modification with SiO_2 and PBT (b) after modification with SiO_2 and PBT.

These films were preliminarily tested for thickness using an Aarson Travelling Microscope (RSP-202) by observing Lycopodium powder on the top and bottom of the film. The thickness was <1mm (~0.5mm). Also, the thickness obtained was verified using ellipsometer where the thickness of 0.6mm was obtained [24].

3.2 FTIR Spectroscopy of CNC/PVA and PVA/CNC film modified with PBT & SiO_2

FTIR plot of PVA/CNC shown in Fig.2 indicated the stretching vibration of OH at 3284 cm^{-1}, which could have offset from the peak of pure PVA. The characteristic cellulosic intra and intermolecular H-bonding has been retained at broad bands between 3600-3000 cm^{-1}.

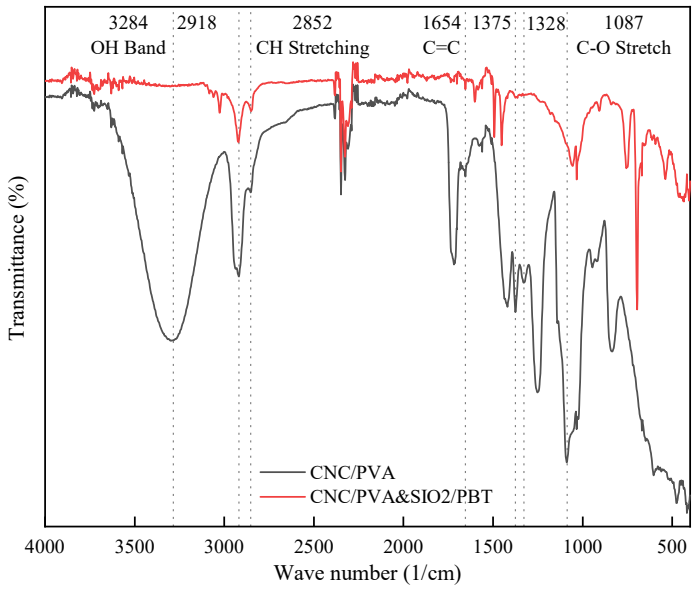


Figure 2. FTIR spectra of a) CNC/PVA composite film (CNC/PVA) and b) CNC/PVA composite film modified with SiO_2 and PBT (CNC/PVA & SIO_2/PBT).

This peak is usually stretched from peaks at 3267 cm^{-1} [17, 33]. The addition of CNC has also resulted in higher intensity stretch at the OH band at 3327 cm^{-1}. Absorption bands at 2918 cm^{-1} and a sharp peak at 2852 cm^{-1} indicate C-H stretching, which indicates alkene's presence, which is also commensurate to CNC/PVA [17, 33]. Bands at 1654 cm^{-1} are for C=C (alkene stretch), along with 1375 cm^{-1}, which might have been shifted from a higher wavenumber due to CNC's addition. Small peaks at 1328 cm^{-1} and 1087 cm^{-1} designate C-O stretching signifying secondary alcohol from PVA, and sharp peaks 1051 cm^{-1} and 1033 cm^{-1} also resemble the same.

The FTIR plot of CNC/PVA & SIO_2/PBT demonstrated specific changes in the peak intensities compared to that of CNC/PVA. The broad peak previously observed at 3284 cm^{-1} is absent, i.e., OH stretch is not retained in FTIR plot of CNC/PVA & SiO_2/PBT. The peak at 2918 cm^{-1} and 2852 cm^{-1} show lower intensity, which indicates the presence of PBT [25,26], while the peak around 1654 cm^{-1} remains intact.

3.3 X-Ray Diffraction of the synthesized CNC

The X-ray diffraction from the samples was shown in Fig. 3. The peaks intensity obtained at 15.457° and 22.678° are designated typically for cellulose II, which has an antiparallel structure

[31]. For the incident radiation, I_{002} plane, the $2\theta = 20.1°$, and $I_{am} = 16.3°$. The crystallinity index (CI) was calculated using equation (1) for those planes, and it was 74.38%, as predicted according to acid concentration during the hydrolysis period. The CI value obtained is comparable to nano-cellulose reported in many works [27, 28, 29, 32]. The small deviations showed is due to the aberrant hydrolysis process.

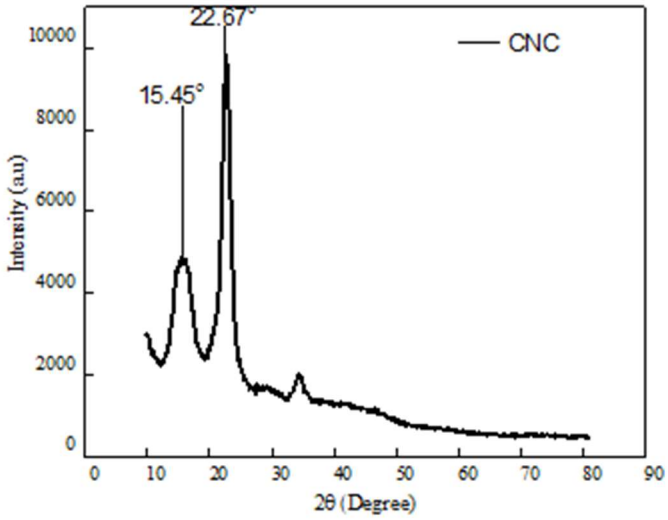
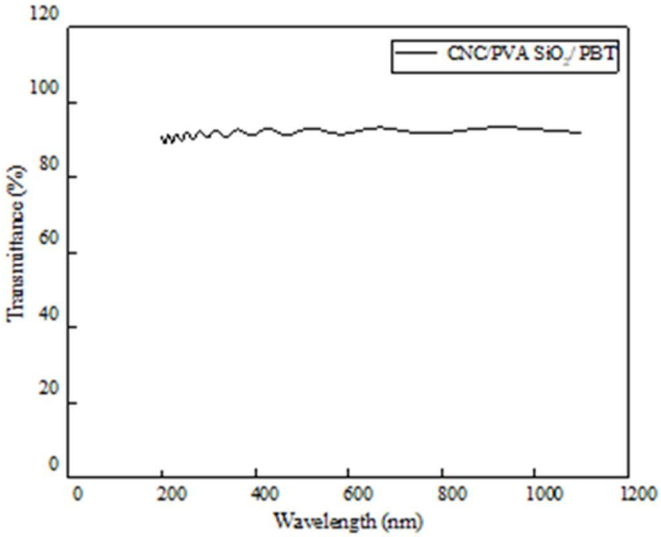


Figure 3: X-Ray diffractogram of CNC powder

3.4 Transmittance Test of the PVA/CNC film modified with PBT & SiO_2

The transparency value was obtained from ellipsometry. Data obtained from the test were plotted against wavelength, and the trend of transmittance from 200 to 1100 nm wavelength is shown in Fig. 4. It was observed that the film transmits consistently over the working spectra range of the solar panel, i.e. (420-700 nm). The result was coherent with the transmittance of traditional PVA/CNC [16]. The average transmittance of 92.18 % in the operating range is low compared to the target (>95 %). This result was observed without chemical treatment or hot-pressing of PVA to obtain high transparency [28].



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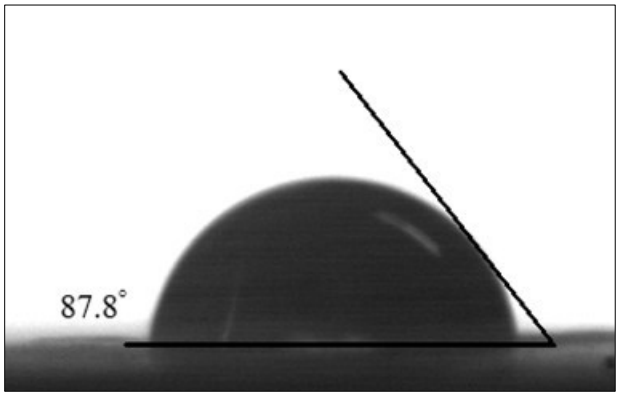
199 **Figure 4**: Transmittance test plot of the CNC/PVA composite film modified with SiO_2 and PBT

200 **3.5 Water Contact Angle Test for the PVA/CNC film modified with PBT & SiO_2**



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202 **Figure 5:** Photograph showing contact angle of test water droplets on PVA/CNC composite films modified with
203 SiO_2 and PBT.

204 The water drop test indicated an apparent average CA of 87.8°. The test was carried out with
205 multiple readings in different directions for a single drop of tap water, as shown in Fig. 5. The
206 readings were averaged to indicate two opposite directions and a total of 4 experiments were made
207 for water CA. They were further averaged to obtain a mean CA of 87.8°.

The water CA was comparatively less than required (>120°) but higher than PET's to enhance the self-cleaning ability of the film [34]. These films also exhibited some wettability, which was qualitatively assessed.

3.6 Durability Test for hydro catalytic and photocatalytic decay of CNC/PVA & PBT/SiO_2 films

The durability test was performed on the prepared PVA/CNC thin-films by exposing it to ambient sunlight for three months in the dry winter season and the photo-catalytic degradation or chemical changes were observed. The film was exposed to 5-7h in sunlight with a glass plate at an inclination of 25° with the horizon facing the true South-East (SE). Similarly, hydrolytic degradation was performed by placing the CNC/PVA thin film in a beaker full of collected rain-water and storing it in a cool dry environment. The FTIR analysis of both samples were conducted and compared with the original plot of fig. 2 and the results were plotted and shown in fig 6. [23].

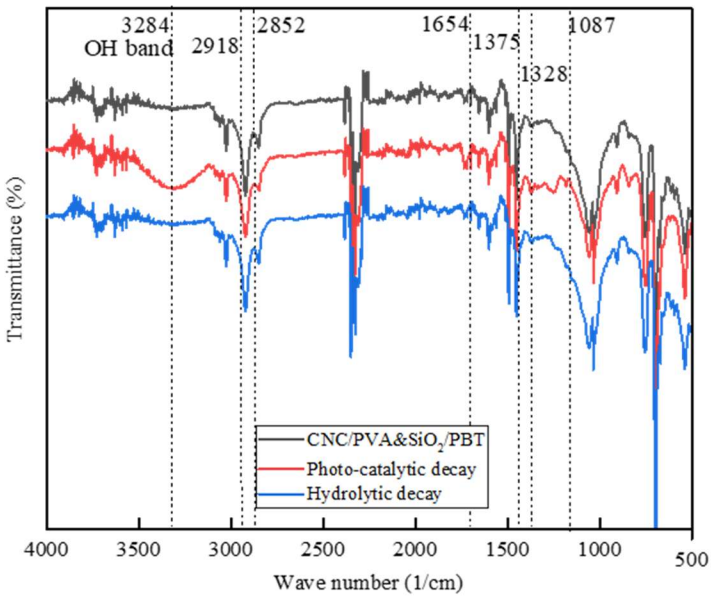

Figure 6: FTIR Spectra of CNC/PVA composite film, CNC/PVA film modified using SiO_2 and PBT, Modified film subjected to hydrolytic decay and Modified film subjected to Photocatalytic Decay.

The stacked plot of individual FTIR plots indicated minimal changes observed in the PVA/CNC modified by SiO_2 and PBT, along with its subsequent degradation in sunlight and water. These

plots showed that the prepared film was resilient against hydrolytic and photo-catalytic action during the study period as there were no significant changes in the characteristic bands for films exposed to sunlight.

Minimum changes were found in the hydrolytic decay. The small broad peak at 3284 cm^{-1} represented the O-H band starting to return to its original intensity. This change could have been because of the degradation of the surface modifiers i.e. silica and PBT in water. The intensity of peaks at 2918 and 2852 cm^{-1} also decreased, implying hydrolytic decay had further affected the underlying substrate of the PVA/CNC film. The same effect was found to be prominent around peaks of 1654 cm^{-1}.

For the photo-catalytic decay, the effect of degradation was minimum. The film retained its PBT coating under ambient air as the O-H band around the 3285 cm^{-1} was not affected. The peaks at 2918 and 2852 cm^{-1} also remained intact, suggesting minimal degradation of the surface modifier i.e. PBT and SiO_2. However, at peaks below 1654 cm^{-1}, the effects were similar to hydrolytic decay, which signified the degradation of the underlying PVA/CNC substrate.

4. Conclusions and Recommendations

PVA and CNC composite films were successfully prepared and modified by silica and PBT to achieve hydrophobicity and transparency by the solution casting method. FTIR tests of PVA/CNC represented characteristic OH stretch at 3327 cm^{-1} and peaks at 2918 cm^{-1} and 2852 cm^{-1} while the composite film had these peaks suppressed, confirming the PBT's and silica's layering effect. The X-ray diffractogram indicated a CI value of 74.38 % which was substantiated for the synthesis of nanocellulose. From this work, following conclusions were drawn:

- The film exhibited an average transmittance of 92.18 % in the range of 420 nm to 700 nm, which was within the optimal range for solar panels to function.
- The water CA of PVA/CNC modified film was 87.8°, which was enough to exhibit hydrophobicity.
- The film showed minimal changes in photocatalytic and hydrolytic degradation during the study period of 3 months, verifying its durability over commonly available coatings.

Finally, the prospect of thin films comprising PVA and CNC with surface modification by PBT and silica as transparent, hydrophobic covers was concluded as promising. Silica-produced

surface roughness in this film could be enhanced further using silanes for better hydrophobicity. Transparency improvement could be accomplished by proper techniques for CNC dispersion and pre-treatment of PVA virtually yielding a transmittance of up to 97% [18]. The ideal film should have a transmittance of ~99% (>95%). In terms of hydrophobicity, a water CA of >120° is required by the surface to successfully exhibit the elusive *Lotus- effect* or self-cleaning property required to counteract solar soiling [6]. Therefore, additional research in this hypothesis could improve suitable properties for better application.

5. References

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