Study of Cellulose Nanocrystals (CNC) & PolyVinylAlcohol (PVA) Polymer Composite Film Modified Using Silica and PolyButyleneTerepthalate(PBT) As a Transparent, Super-Hydrophobic, Self-Cleaning Cover

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Abstract

Solar panel soiling is a major barrier in electricity generation by solar Photo-Voltaic (PV) technology, especially in dust-prone cities like Kathmandu. Currently employed techniques use expensive cleaning bots, short-lived coatings or environmentally non-friendly coatings. This paper encompasses a study of a green alternative to counteract solar panel soiling. Cellulose nanocrystals (CNC) blended with Poly Vinyl Alcohol (PVA) with surface modification by Poly butylene terephthalate (PBT) and powdered silica was used to produce a transparent, hydrophobic film which could act as a self-cleaning cover for soiling prone solar panels. The film exhibited an average transmittance of 92.18% of the incident light in the solar PV working spectra (420nm-700nm). Hydrophobicity was quantified by the water contact angle (WCA) which was an average of 87.25°. The film was durable to photocatalytic and hydrolytic decay but further research is warranted before rendering the film suitable for use as a protective cover for solar panels.

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 Photo-Voltaic (PV) panels has been a growing field of study. As we begin the second decade of the 21st century, solar panels have not only been an eco-friendly, regenerative form of energy and has become the source of income. This second decade is set to improve solar power generation in terms of cost per watt, making solar power affordable for application [1]. Solar power is harnessed using small modules of silicon p-n junction

semi-conductor called PV cells, which trap solar radiation, generally in the range of 420 to 700nm wavelengths. The common and commercial silicon PV is capable of capturing up to 800nm wavelength of light [2]. The major problem associated with this energy conversion is the blockage of these panels by soiling. Solar panels are vulnerable to soiling by dust (particulate matter), bird's dropping, dew etc. It becomes a nuisance especially in dust-prone cities, where the applications include street lightning, rendering timely maintenance difficulty and costly. In a dust-prone city like in the Kathmandu valley, soiling induced transmittance losses up to 69.06% and a power loss of 29.76% owing to a dust deposition density of 9.6711 g/m^2 over a study period of 5 months in the dry season [3].

For timely maintenance against solar soiling, cleaning robots are used, which are latched onto and move along the array of panels are, especially in large solar farms. This is quite effective for areas with high soiling rates. Some make use of sprinkler systems while some use commercially available anti-soiling coating solutions [4,5]. Commercial coatings like fluorinated silanes are often used for anti-soiling but the disadvantage of such coatings lies in the durability, that they dissipate rather quickly when exposed to atmosphere. Durability on weathering or exposure to conditions of thermal and moisture induced stresses in the coating reducing its durability. This leads to decrease in primary traits where the hydrophobic coating are used which makes the coating usable i.e. hydrophobic [6,7]. Economically, this becomes expensive as it needs to apply the coating periodically. Some commercial coatings in practice are non-biodegradable inorganic materials such as TiO_2-Fe_2O_3 [8] which is detrimental to the environment. So, a green alternative for the coatings is needed. Since the durability of coatings comes into question, eco-friendly super hydrophobic "thin-films" was the key area of this research. Thin-films (<1mm) could be used as a protective cover layer for solar panels. The versatility of the film could technically be used for applications where "self-cleaning" and dust repelling properties are required.

The self-cleaning property of these films is a consequence of the "Lotus-effect". When a surface is sufficiently super-hydrophobic, water droplets rolls on the surface carrying away any foreign particle (dust) along with it. Inherently hydrophobic materials like Polyethylene terepthalate (PET) in its pristine form exhibits a WCA of $75.3^{\circ} \pm 1.2^{\circ}$ [9]. For inherently hydrophobic films or even hydrophilic films to reach super-hydrophobicity (WCA>120°), surface modifications are needed. By creating micro- and nano-corrugations on the surface of these films, one can achieve super-

hydrophobicity. These corrugations result in either 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 can be conducive to achieve a range of surface modification from hydrophilicity to hydrophobicity on a substrate along with the CB state required for certain applications [12, 13]. This also reduces 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 (super-hydrophobicity by surface modification), low dust-water affinity (low surface energy) and near-perfect transparency is required for the thin film.

In recent history, CNC have shown to be a very versatile material when it comes to application and polymer synthesis. CNC have also been known for its all-rounded physical and chemical properties, depending upon the process and source of its formation. Highly crystalline nanocellulose can be formed by agitating cellulose chemically or mechanically [14,15]. Acid hydrolysis is a common method for chemically synthesizing CNC while mechanical methods involve processes like roller mechanical technique, compression mechanical technique, cryocrushing, sonication, homogenization and so on [15, 27]. CNC are best for this application because of its versatility in polymer making, easy procurement, manufacture, eco-friendly nature and the ability to manipulate physical and chemical properties as per need [16]. Poly vinyl alcohol (PVA) is a water-soluble material commonly used as adhesives. PVA has good chemical resistance, optical properties and is easily available. Further, using CNC as a filler for making PVA films, its water absorption will be reduced [17] making it easier to modify its surface for hydrophobicity. The dispersion of CNC in PVA is critical to determine its physio-chemical properties. Durability is a property common with the use of CNC/PVA in packaging [16] which is advantageous compared to coatings and by changing PVA/CNC concentrations, the proper transparency or most specifically an appreciable transmittance (>95%) in the solar PV working range (420-700 nm) can be attained [17, 18]. Even though PVA is traditionally cloudy (not transparent) in water, methods such as hot-pressing or chemical treatments can improve its transparency to near perfection [18]. As, per CNC, transmittance and optical haze can be improved by increasing the crystalline content (more CNC in the matrix) [19]. Moreover, the added benefit of cost-effectiveness makes PVA/CNC an ideal combination.

2. Experimental

2.1 Materials

For the CNC preparation, Micro-crystalline cellulose (MCC) with 98% purity and particle length ranging from 20µm to 100µm was purchased from Bandana Trade Concern (BTC), Lalitpur, Nepal. 95% by wt. sulphuric acid (H_2SO_4) was provided by Nano-materials laboratory at Institute of Engineering, Pulchowk Campus (Lalitpur, Nepal). PVA with a degree of hydrolysis and a molecular weight of 83000 g/mol was also purchased from BTC. Toluene was used as a solvent for surface modification and was procured from Eureka International Enterprise (Kathmandu, Nepal). Silica gel-g was obtained from Eureka. Miscellaneous chemicals used in the preparation was provided by nano-material laboratory of Institute of Engineering (IOE), Pulchowk and were of laboratory grade. In this work, chemicals were used without 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 key to obtain appropriate properties of the prepared CNC. Longer hydrolysis time renders the breaking of coarse aggregates in the cellulose matrix of CNC leading to larger axial ratios of the CNC. This yields lower elastic modulus and hardness values [21]. Larger axial ratios also attributes transparency [19].

50g of MCC was mixed with 50ml of de-ionized distill water and subjected to drop wise addition of 500ml of 64% by wt. H_2SO_4 for a hydrolysis time of 1h. The hydrolysis was carried out in a temperature maintained at 45°C with a magnetic stirrer operating at 200-600 rpm, depending upon the viscosity of the mixture [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 suspension of CNC settled, the supernatant liquid was decanted off and the sediment was kept for further purification. CNC at this time was highly acidic. To make CNC acid free, 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 each at replacement batch until the pH was approximately 6.53 (~7) measured using a Measuretech PHS-3C digital pH meter[16,19]. To separate unreacted MCC in the suspension, a 0.22µm Whatman membrane filter was used in a vacuum filtration process using a Joan VT335, vacuum filtration apparatus [22]. The filtrate obtained, characterized

by opalescence in appearance is the prepared CNC. The solution was kept at 5°C freezer for storage and 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°C for 5h for complete dissolution, using a magnetic stirrer at 800 rpm [23]. The PVA/CNC blend was created by using a mixture of 80% PVA, 15% CNC suspension and 5% Glycerol. Glycerol was added to improve dispersion of CNC in the mixture. CNC concentration was conducive to modify for hydrophobicity in the later process [17]. The mixture was kept at 60°C and stirred for 30mins at 800 rpm.

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

2.4 Surface Modification

1g of silica-g with 2g of finely crushed Poly butylene tereapthalate (PBT) was dissolved in 20ml of anhydrous Toluene. The suspension was ultra-sonicated for 10mins at 25°C. 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. The assumption being 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} 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 exposed to photocatalytic and hydrolytic media.

The X-ray diffraction data was 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 was prepared by freeze-drying the

suspension at -40°C of CNC via BIOBASE BK-FD10S Laboratory Freeze Drying Vacuum Freeze Dryer/Lyophilizer at Nano-Lab IOE, Pulchowk [28, 29].

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

Drop test was conducted at 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 opposite ends.

3. Results and Discussion

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 looks good. The film lacked inconsistency in concentration unlike solution-casted films and were easy to peel off from the substrate unlike glass-substrate films. These films were analyzed by different techniques. Fig. 1a and b are the macroscopic photographs of these films.

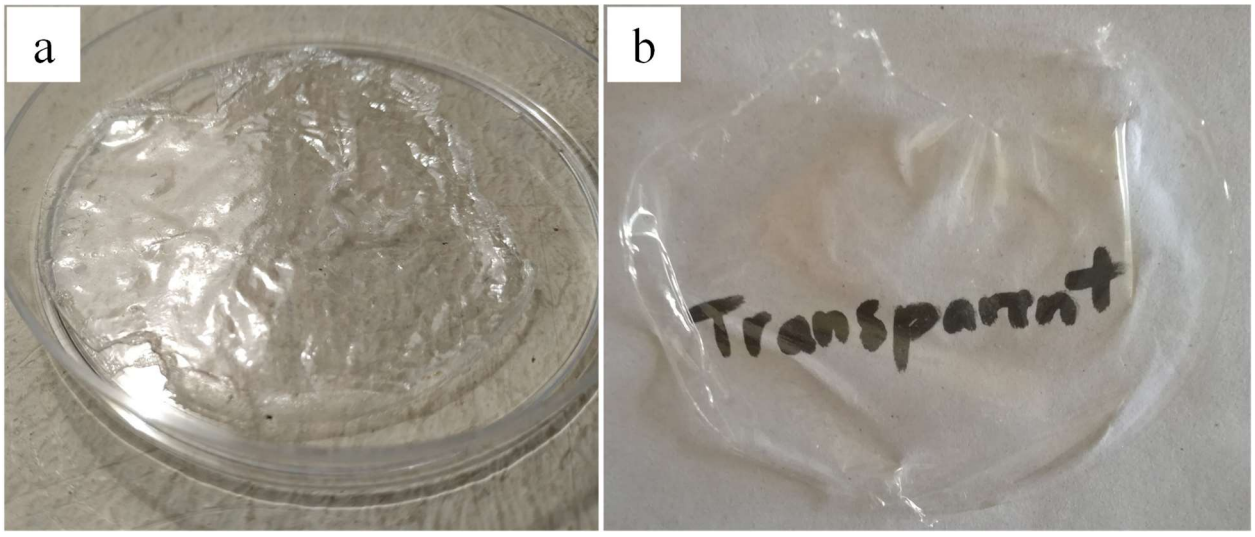

Figure 1. Prepared CNC/PVA film (a) before modification with SiO_2 and PBT (b) after modification with SiO_2 and PBT.

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].

FTIR Spectroscopy

From the FTIR plot of CNC/PVA, the stretching vibration of OH can be seen at 3284 cm^{-1}, which could have offset from the peak of pure PVA. The characteristic cellulosic intramolecular and intermolecular H-bonding has been retained at broad bands between 3600 - 3000 cm^{-1}.

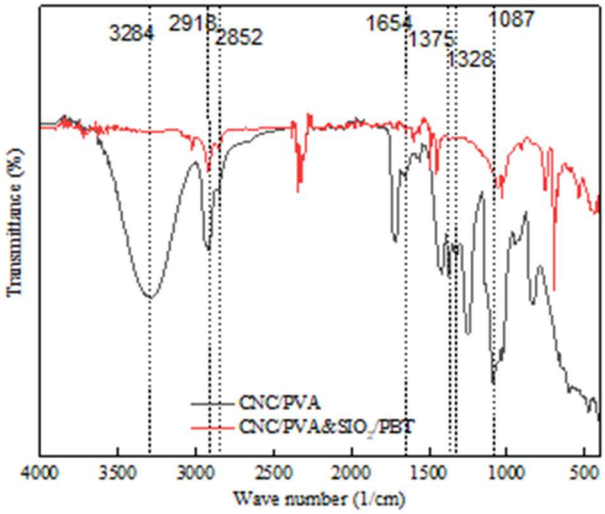

Figure 2. FTIR spectra of a) CNC/PVA composite film (CNC/PVA) and b) CNC/PVA composite film modified with SiO_2 and PBT (CNC/PVA & SIO_2/PBT).

This peak is usually stretched from peaks at 3267 cm^{-1} [17, 33]. Addition of CNC has also resulted in higher intensity stretch at the OH band at 3327 cm^{-1}. The absorption bands at 2918 cm^{-1} and sharp peak at 2852 cm^{-1} indicate C-H stretching which indicates the presence of alkene which is also commensurate to CNC/PVA [17, 33]. Bands at 1654 cm^{-1} is for C=C (alkene stretch) along with 1375 cm^{-1} which might have been shifted from a higher wave number due to the addition of CNC. 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 same.

The FTIR plot of CNC/PVA & SIO_2/PBT demonstrated certain changes in the peak intensities as 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 present of PBT [25,26], while the peak around 1654 cm^{-1} remains intact.

X-Ray Diffraction

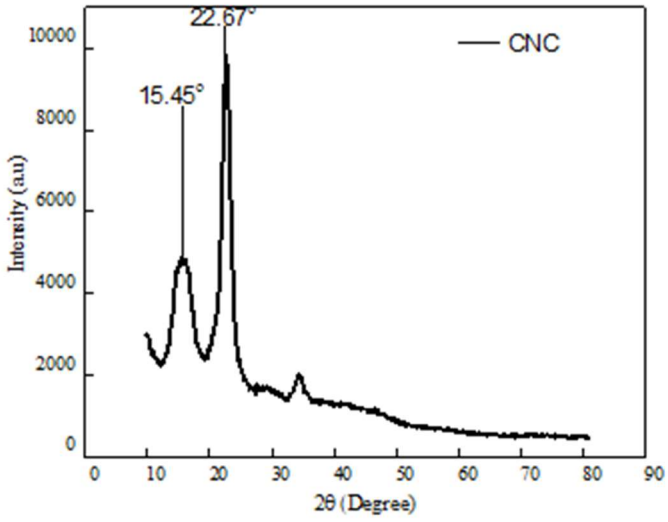

Figure 3: X-Ray diffractogram of CNC powder

The intensity of X-ray radiation refracted out from the samples was plotted as shown in Fig. 3. The intensity peaks obtained at 15.457° and 22.678° are designated typically for cellulose II, which has antiparallel structure [31]. For the incident radiation, I_{002} plane, the $2\theta = 20.1°$ and I_{am} is 16.3°. The crystallinity index (CI) was calculated by using equation (1) for those planes and it was 74.38%, as predicted according to acid concentration during hydrolysis period. The CI value obtained is comparable to nano-cellulose reported in many literatures [28, 29, 32]. The small deviations showed is due to the aberrant hydrolysis process.

Transmittance Test:

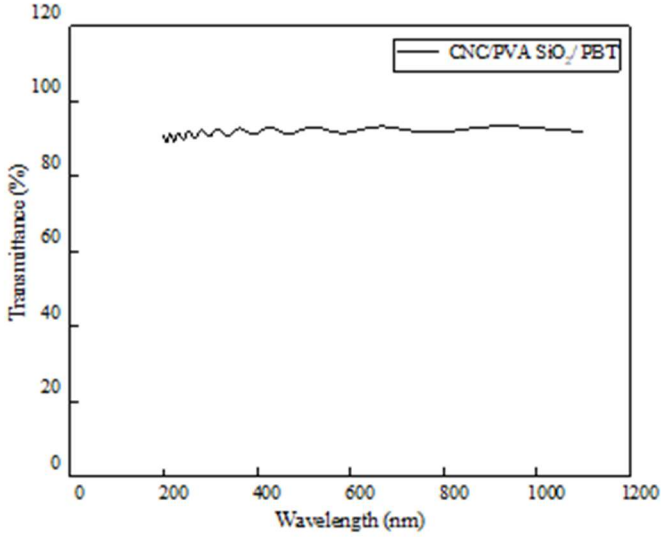

Figure 4: Transmittance test plot of the CNC/PVA composite film modified with SiO_2 and PBT

The data points obtained from ellipsometry were plotted against wavelength. The trend of transmittance from 200 to 1100nm wavelength is shown by the scatterplot in Fig..4. It can be observed that the film transmits consistently over the working spectra range of the solar panel i.e. (420-700nm). The result is consistent to transmittance of traditional CNC/PVA [16]. The average transmittance of 92.18% in the working range is low compared to the target (>95%). But this was obtained without chemical treatment or hot-pressing of PVA to obtained high transparency. [28]

Water Contact Angle Test

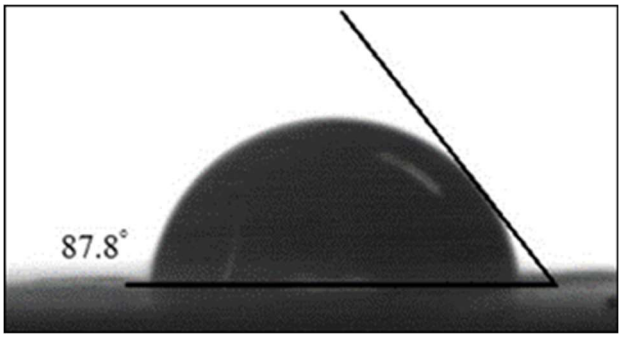

Figure 5: Photograph showing contact angle of test water droplets on PVA/CNC composite films modified with SiO_2 and PBT.

The water drop test indicated an apparent average WCA of 87.8°. The test was carried out with multiple readings in different directions for a single drop of tap water, as shown in the Fig. 5. The readings were averaged to indicate two opposite directions "Left" and "Right" and a total of 4 drops were measured for WCA. They were further averaged to obtain a mean WCA of 87.8°.

The WCA is much less than the required (>120°) [34] to enhance the self-cleaning ability of the film. These films exhibited some wettability which was qualitatively assessed. Further, the sample were not subjected to further testing of sliding angle (SA) which is also a key parameter in determining hydrophobicity.

Durability Test

The durability test is performed on the thin-films by exposing to the ambient sunlight for a period of three months of dry winter season to assess the photo-catalytic degradation or chemical changes in the CNC/PVA films. The films were exposed to 5-7h of sunlight by being placed on a glass plate at 25° inclination 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 i.e. Fig. 2. [23] as shown in Fig. 6.

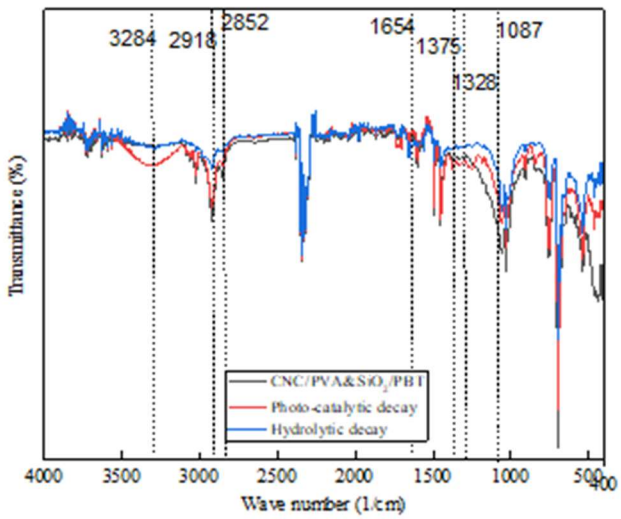

Figure 6: FTIR Spectra of CNC/PVA composite film, CNC/PVA film modified using SiO_2 and PBT, Modified film subjected to hydrolytic decay and Modified film subjected to Photocatalytic Decay.

From the Fig. 6, the stacked plot of individual FTIR indicates changes made in the composition of CNC/PVA modified by SiO_2 and PBT, along with its subsequent degradation in sunlight and water. From the plots of CNC/PVA & SiO_2/PBT, photo catalytic decay and hydrolytic decay, it can be observed that minimal changes take place between the three. This suggests that the prepared film has resilience against hydrolytic and photo-catalytic action during the period of study.

In the Hydrolytic Decay plot, the small broad peak at 3284 cm^{-1} which represents the O-H peak starts to take shape. This could be because of the degradation of the surface modifiers i.e. silica and PBT in water. The peaks at 2918 and 2852 cm^{-1} shortened, (less intense) implying that hydrolytic decay has further affected to the underlying substrate of PVA/CNC. The same effect is prominent around peaks of 1654 cm^{-1} and less.

For the photo-catalytic decay, the effects of degradation are minimum. Under the ambient air, the film retains its PBT coating as the O-H plain around the 3285 cm^{-1} is retained. The peaks at 2918 and 2852 cm^{-1} also remains intact suggesting minimal degradation of the surface modifier i.e. PBT and SiO_2. However, at peaks below 1654 cm^{-1} the effects are similar to hydrolytic decay, which signifies the degradation of the underlying CNC/PVA substrate.

Conclusions and Recommendations

CNC and PVA composite films were successfully prepared and further modified by silica and PBT to achieve hydrophobicity and transparency. The films were created using the solution casting method. FTIR tests of CNC/PVA represented characteristic OH stretch at 3327 cm^{-1} and peaks at 2918 cm^{-1} and 2852 cm^{-1} confirming the presence of PBT and success of the coating process. The X-ray diffractogram indicated CI value as 74.38% which is substantiated for the synthesis of nanocellulose. From the results following conclusions were drawn:

- The film exhibited an average transmittance of 92.18% in the range of 420nm to 700 nm which is the optimal range for solar panels to function.
- Hydrophobicity estimated on the basis of WCA for the final CNC/PVA modified film was around 87.8° contact angle measured using water drop test.
- Results from photo catalytic and hydrolytic degradation tests showed minimal changes in the film's composition over a study period of 3 months. It can be concluded that the film is durable than the commercially available coatings.

Finally, the thin film comprising CNC and PVA with surface modifications by PBT as a thin hydrophobic layer and Silica as a surface roughness inducer produced by the methods described in this study is promising. In this film the transparency can be improved by proper techniques for CNC dispersion and pre-treatment of PVA for transparency which could possibly yield a transmittance of up to 97% [18]. The ideal film should have a transmittance of ~99% (>95%). In terms of hydrophobicity, a WCA of >120° is required by the surface to successfully exhibit the elusive "Lotus- effect" or self-cleaning property required to be used as a cover for solar panels. Better surface reactants like silanes can be used further to increase the hydrophobicity to a contact angle greater than 120°. [6]

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