CELLULOSE/GRAPHENE-OXIDE ORIENTED COMPOSITE FOR PHENOL REMOVAL FROM AQUEOUS SOLUTIONS: FORMULATION AND ANALYSIS

[1]Dr.E.SAROJPURANI

[1]ASSISTANT PROFESSOR, Department of CHEMISTRY

Sri Manakula Vinayagar Engineering College, Madagadipet Pincode: 605107.

Puducherry, India

E-mail ID : sarojpurani@gmail.com

Orcid id: 0009-0002-4716-6983

[2]Dr.S.SAVITHIRI

[2]PROFESSOR, Department of CHEMISTRY, Sri Manakula Vinayagar Engineering College, Madagadipet, Pincode: 605107, Puducherry, India

E-mail ID: harishoct52007@gmail.com

Orcid id: 0009-0006-4535-9705

[3]SATHESHKUMAR G K

[3]Assistant Professor

Department of Civil Engineering, S.A Engineering College

Avadi poonamallee high road,veera ragahavapuram, Thiruverkadu, Chennai -77

Thiruvallur, Tamilnadu, India

E-mail ID – satheshkumargk@saec.ac.in

Orchid id- 0000-0003-4245-2905

[4]D. T. Sakhare

[4]Assistant Professor

Department of Chemistry

U.G., P.G. & Research Centre, Department of Chemistry, Shivaji Art's, Comm. & Science College Kannad Dist. Aurangabad 431103 Maharashtra India

Email id: sakharedhondiram@yahoo.com

ORCID ID: 0000-0003-0242-9516

Abstract: In this research, freeze drying was utilised to remove excess water from wet CNF and CNF-PF composite films, which sped up the processing time and made the films wrinkle-

free. The nanocomposite was manufactured by heating the freeze-dried sheets. Primary physical and mechanical factors were evaluated in addition to the morphology. Discontinuous patches, possibly voids generated by low-temperature drying, can be seen in both CNF and CNF-PF complex films. Both films show these gaps. The films are both supple and robust since the adding of PF has a negligible impact on the mechanical strength of the material. The mechanical asset of a film is often diminished after being freeze dried as opposed to oven dried. Freeze-drying CNF and CNF-based nanocomposites can be an efficient method of preparation when time is of the essence.

Keywords: phenol formaldeyde (PF); nanocomposites; mechanical strength; cellulose nanofibrils (CNF); freeze dry.

I. INTRODUCTION

As people develop more aware of the position of defensive the setting, they increase their reliance on biomass and biomaterials. With a yearly growth rate of 1.5 x 1012 metric tonnes [1], cellulose remains the greatest copious usual reserve on Earth. The theoretical modulus of cellulose's smallest fibres, termed microfibrils, is greater than 150 GPa [2]. By repeatedly subjecting pulp fibre to high-speed shear, a novel cellulosic material was developed in the early 1980s [3, 4]. Microfibrils and aggregates of microfibrils formed as a result. Cellulose nanofibrils (CNF) was the more popular name for this high-performance cellulose variant [5], but the word "microfibrils" is now more commonly used.

Depending on the defibrillation methods and the starting fibres, the resulting cellulose nanofibrils have widths (or diameters) of less than 100 nm. Taking readings in the microsecond or micromillimeter range. CNF produced are solvent- and water-soluble, unlike cellulose, and form a stable gel structure at low concentration [6]. Nanofibrils are able to interconnect in solution and after drying because of their high aspect ratio (greater than 100) and abundance of surface hydroxyls. CNF is a crucial reinforcing component in nano- or bio-composites [7-8] due to its unique tangling activity. In addition to its superior mechanical Applications for cellulose nanofibrils abound [9] because to their robustness, high aspect ratio, and sizable surface area.

Hydrophilic groups on CNF, especially hydroxyls, became much more accessible once interfibrillar hydrogen bonding was broken. Consequently, both the dry plain materials and the composites on which they are based are highly reactive to the presence of water and moisture, and can absorb substantially more water than their initial weight. When nanofibrils

absorb water, they expand, and the bonds between them are replaced by those between the water molecules and the nanofibrils themselves. The material's mechanical strength plummets and its gas-barrier properties shift as a result of this process. High performance composites' water resistance was improved with the use of water-proof mastic or aquaphobic polymers also CNF [10, 12]. In a wide range of conditions, Henriksson and Bergland found that composite films made from CNF and melamine formaldehyde (MF) absorbed relatively little water. We compromised on durability since melamine formaldehyde resin is so brittle. The CNF/PF nanocomposites are produced by filtering a mixture of PF resin and a CNF suspension, then drying the mixture in an oven, and finally pressing it under high heat. The addition of PF resin barely budged the mechanical strength. However, it is not very fragile in wet environments [11, 12].

It is difficult and time-consuming to remove water from CNF or CNF-polymer suspension systems. When the water concentration of a material is reduced, the widely scattered nanafibrils gather together as a result of capillary forces and, ultimately, the strong cooperative hydrogen link between hydroxyl groups [13]. Without preventative measures, such as external pressure, the aircraft will rapidly contract due to the enormous collapse and attraction, and the space for the films will become severely wrinkled. Solution casting is advantageous since water evaporates gradually at normal temperature. The produced films are not flat even after extensive processing due to the force of surface tension. Here, we analyse the morphological, physical, also mechanical performance of CNF also CNF/PF wet films and present a novel technique for eliminating excess water from these materials by freezing them.

II. MATERIAALS AND METHODS

In this study, cellulose nanofibrils that had been oxidised with TEMPO were synthesised using the protocol published . The pulp fibres were homogenised in a disperser after being washed with distilled water to remove any leftover oxidation and prior to separation. We separated the coarse and fine fractions by diluting the fibre slurry and centrifuging it at 12000 g, with the coarse fraction being thrown away. Once the solid content of the nanofiber suspension was down to about 0.4%, it was ultrafiltered. Microfluidics M-110EH-30 Microfluidizer (series of 200 and 87 m chambers; Microfluidics; Newton, MA) was used to process the nanofiber suspension once. The PF resin that was used in this instance was provided by Georgia-Pacific LLC. It was a product that was readily available on the market

and had a solid percentage of 50.5%. This particular type of resin is typically used in the production of fiberboard and particleboard.

A. Making Composite Nanofiber and Polymer Films

Before manufacturing CNF films, a well-distributed nanofiber suspension was made by reducing the concentration of CNF slurries from 0.4 wt% to 0.2 wt% and agitating the mixture by hand for one hour. Distillate water was used in this process. We blended PF resin that had been diluted in water (at concentrations of 5%, 10%, 15%, and 20% respectively) with a CNF solution in order to produce CNF/PF nanocomposites. By means of a lyophilization equipment manufactured by Labconco , the rainy CNF also CNF/PF pictures were subjected to a vacuum of 0.01 MPa and a refrigeration coil temperature of -60 oC used for the duration of the 8 hours that followed the separation of the nanomembrane from the CNF and CNF/PF films. After being lyophilized, the films remained placed in a humidity room for three days where the temperature was maintained at 27 degrees Celsius and the relative humidity was kept at 65%. After treating the films, they were sandwiched in between two plates made of stainless steel and subjected to heating for three minutes at a temperature of 130 degrees Celsius and 30 MPa. The completed films and composites had a diameter of 120 millimetres and a thickness that ranged from 0.09% to 0.12% millimetres.

B. Gauging Density and Microporosity

Dogbone-shaped examples were trained at 27 °C also 50% relative humidity used for additional than 48 hours to determine the densities of films also amalgams. Using a piece of calibrating equipment (an AG104 from the Swiss company Mettler Toledo), the sample weights were determined to within four fraction places (0.0001g). Density remained determined by plugging values into the formula =m/v. The symbols m and V are used to denote the density, mass, and volume of a specimen. At least five specimens were analysed from each sample. To calculate porosity from the above density values, apply the following equation.

$$\text{Porosity} = (1-\rho_{com}/\rho_{cel})\times 100\% \text{ -----1}$$

Where com and cell stand for the composite film's density and the density of pure cellulose, respectively (1500 kg/m3).

C. Performing Under Tension

Using ASTM D638-10, the tensile characteristics of CNF also CNF/PF nanocomposite films remained determined. Die cutting was utilised to create the standard dogbone shape

according to ASTM D638-10. Before being put through their paces, every sample was conditioned for a week in a lab at 50% RH and 27 °C. Using a 500 N load cell and an Instron 5865 universal materials testing machine, we conducted the test at a regulated relative humidity of 50% and temperature of 23 °C. Preloading the specimens to 10 N and moving them across the head at 1 mm/min successfully reduced slack. For each criterion, at least 5 samples were evaluated. Using the cross-head displacement and the narrowest part of the dog-bone samples, the gauge length was calculated. The modulus of elasticity was determined using the elongation at break at 71% of the thoroughgoing harvest pressure (30-70 MPa).

III. RESULTS AND DISCUSSION

Since the separated CNF also CNF/PF films retain 15-20% particles after passing through the filtering membrane, rapid evaporation of water from these films would result in significant shrinkage and wrinkling in the dried films. However, although it takes a full week to complete, slow water drainage is more practical for drying films without creases. From a business standpoint, these are undesirable because to the high processing time. Freeze drying (which takes 6 hours to finish under the same conditions) is an efficient way of eliminating water with little shrinkage and deformation from the aforementioned films.

A. Appearance and Functionality

The various layers that are included in CNF films make it easier for substances to pass through the gaps between them. Studies using a SEM on the surface of the crack as well as its cross section demonstrate this new structure. When the water is filtered, the nanofibrils that were suspended in the CNF-containing water fall to the filter and settle there. Because the nanofibrils are so minute and are packed so closely together, CNF films give the appearance of being transparent. The TEMPO oxidised CNF sheets have a thickness of 40 metres and have the potential to allow up to 90 percent of light with a wavelength of 600 nanometers to pass through. Previous studies have revealed that the chemical characteristics of PF resin experienced only a slight decline when stored at extremely cold temperatures (16 °C). This was demonstrated by the fact that the chemical properties of PF resin were not affected at all. Figure 1 displays examples of films that are composed of CNF and CNF composites that contain 10% by weight of PF. Because the dried films were wrinkle-free and smooth, freeze drying proved to be an efficient strategy for reducing the considerable collapse that occurs when water is removed from CNF wet films. This was evidenced by the fact that the films were smooth after they had been dried. The formation of the microscopic

spots that were observed in CNF and CN/PF films did not occur in films that had been dried in an oven. Since spots are difficult to delaminate, it is believed that they are a reflection of newly formed voids between surrounding nanofibrils. There could be a number of reasons for this, including the capability of the freeze mechanism to prevent hydrogen bonding and any partial collapse that might otherwise take place. Loss in mechanical stability and visual light transmission shouldn't come as much of a surprise, nor should the building's unappealing aspect come as much of a surprise. However, additional research is necessary in order to determine where this unusual pattern first emerged from.

Fig 1: Samples of CNF also CNF/PF films' visual presentation

B. **Mechanical and Physical Characteristics**

Key physicochemical and mechanical parameters of freeze-dried CNF also CNF/PF films remain reported in table 1, and illustrative strain-stress curvatures are shown for together film types in FIG. 3. The CNF also CNF/PF amalgamated films remain spongy, despite their versatility and durability. It's worth noting that the fracture strain values documented here range from 13 to 16%, which is higher than the numbers provided elsewhere in the literature. It's a big step higher over, instance, the CNF/MF compound films created [10]. This difference is far larger than three times as large. Strain at failure obtained is similar to that of films made from highly polymerized cellulose nanofirils .

It's possible to explain this phenomenon in a variety of ways. The TEMPO-oxidation process is the backbone of the defibrillation technique, as it produces ultrafine nanofibrils with a consistent diameter and a high aspect ratio. This is achieved by applying a repulsive force on the area in question. Under these conditions, the crystalline and molecular structures were mostly unaltered. Having all of these advantages after the films have been created will help to improve their mechanical strength. When combined with the material's density, it provides a meaningful measure of the composite's ability to withstand mechanical stress. The

composite material's density is also an important parameter for evaluating its ability to withstand mechanical stress.

Considering that tightly packed nanofibrils are likely responsible for forming a dense overall structure. The porosity of CNF/PF composites reduced with increasing PF concentration, especially for PF weights in the 5-10% range. Figure 3 shows this pattern. This result corroborates the hypothesis that less empty spaces were present in the CNF film after PF molecules were incorporated into its fibrous structure. Due of its low density (1300 kg/m3 compared to 1500 kg/m3 for cellulose), however, PF's porosity is reduced as the dosage is increased. When a composite is subjected to continuous stress, the PF resin remains expected towards operate as fillers to slide and mend cracks also microflaws, in addition to increasing adhesion between nanofibrils. This is because PF resin has the ability to both mend and slide.

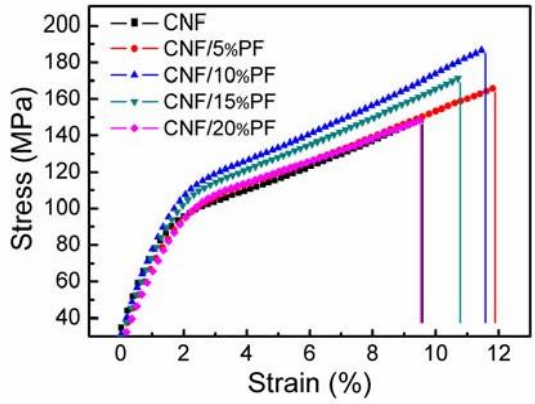

Fig 2. CNF and CNF/PF composite film strain-stress curves are typically as follows:

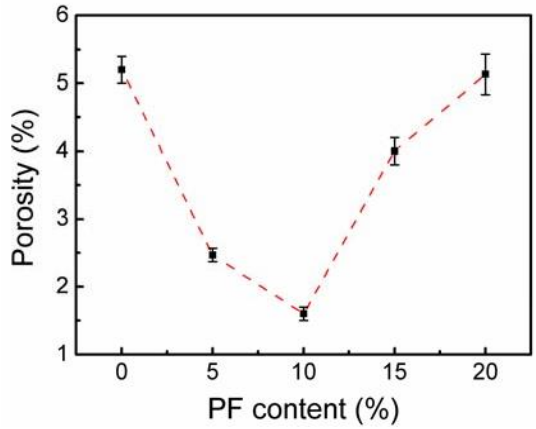

Fig 3. Combined CNF and CNF/PF film permeability

Table 1. CNF and CNF/PF Complex Films' Primary Mechanical and Corporal Possessions

Materials	**Density**	**Stress at break**	**Strain at break**	**Modulus**	**Work of Fracture**
(CNF/PF, W/W)	**(kg/m^3)**	**(MPa)**	**(%)**	**(GPa)**	**(MJ/m3)**
100/0	1523 (16[a])	159 (18)	14.7 (1.3)	3.2(0.4)	7.9 (0.7)
95/5	1564 (12)	176 (12)	18.0 (1.0)	2.9 (0.2)	6.0 (0.6)
90/10	1577 (20)	198 (17)	17.5 (1.7)	3.5 (0.3)	8.7 (0.6)
85/15	1541 (15)	182 (10)	16.4 (1.4)	3.3 (0.2)	8.6 (0.5)
80/20	1524 (21)	159 (19)	14.6 (1.7)	2.9 (0.4)	7.6 (0.7)

The results of an analysis of variance (ANOVA) performed on the data gathered show that the addition of PF resin normally has no impact on the tensile asset of the material. However, according to the statistical analysis (=0.05), the mechanical strength of the complex films with 10% also 15% PF solid fillings is significantly greater than that of the neat ones. This is as a consequence of the fact that the results of the density and porosity tests disclose the appropriate structure following the introduction of PF at specific levels. As a result of the low moisture content, the composite films are delicate, and cracks started to emerge in the samples as they were being made while they were still in the manufacturing process. Since the formation of microscopic cracks in films of this thickness is a rather simple process, one may easily ascertain the film's ultimate strength. It's possible that you'll need to laminate many film layers in order to get an accurate reading on the motorized strength of such soft resources.

C. **Direct Evaluation of Mechanical Power**

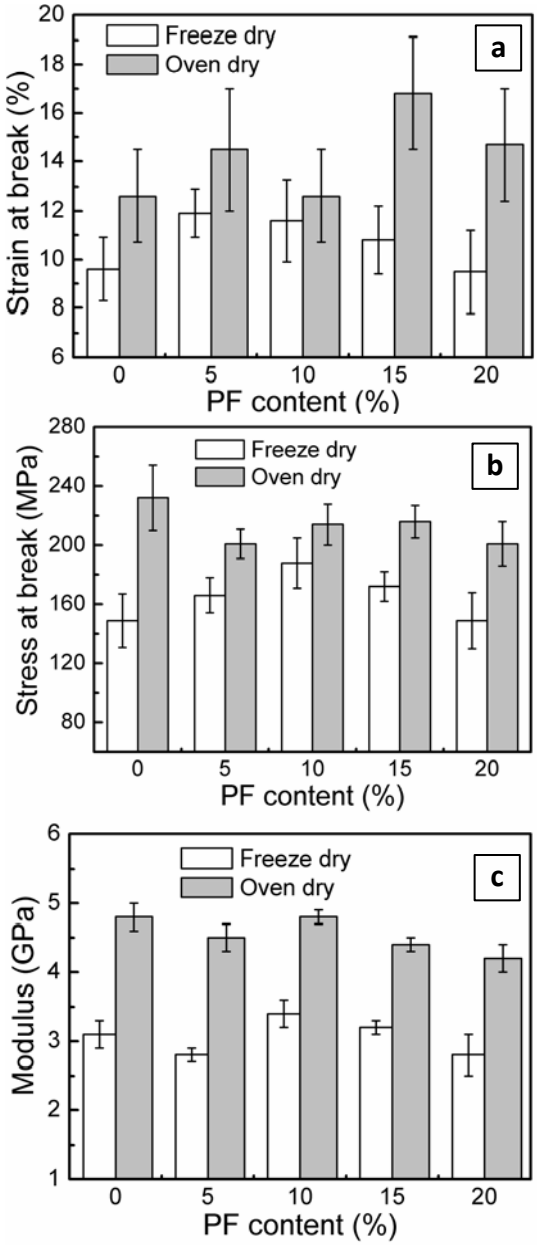

Fig 4. a, b, and c denote strian at break, stress at beak, and modulus, individually; a, b, and c are similar between freeze-dried (open colums) and oven-dried (filled colums) CNF also CNF/PF films.

The freeze-dry method's mechanical strength was measured against that of the oven-dry method to gauge its efficacy. Oven dry was proposed with a thorough description in reference [11]. In a nutshell, after filtering, wet films made of CNF or CNF/PF were sandwiched amongst waxy covered paper also filter paper to wick away additional

moisture. In addition, a lift of around 23 kilogrammes was applied to the assembly in order to minimise film distortion. When the percentage of solids reached 80 to 90%, the sandwiched films were baked at 60 degrees Celsius for 8 hours to dry them off. This method is identical to the freeze-dry one. Strain at break, stress at break, and modulus were compared between the two process conditions and depicted in Fig. 4. The mechanical strength of composite films produced in an oven is clearly superior. Freeze-drying substances at extremely low temperatures (-30 oC) is the most likely cause of this phenomenon because it inhibits the collapse of molecules and the formation of hydrogen bonds. Consequently, the mechanical strength is decreased because to the relatively weak bonding. Since freeze drying cuts down on processing time, it can be used to make CNF and CNF-polymer composite films without worrying about them shrinking or wrinkling.

IV. CONCLUSIONS

Wet films were freeze dried to eliminate excess water; this took very little time and produced a wrinkle-free final product. However, the discontinuous patches seen in CNF also CNF-PF merged films are thought to be related to the films' low infection drying. The films are both elastic and durable, but the incorporation of PF has virtually little effect on their mechanical robustness. When associated to oven-dried films, the mechanical strength of freeze-dried films is lower. Freeze drying is a fast and efficient method for producing CNF and composites from it. This promising first result emphasises the need for additional research into the causes of the unusual structure and reduced mechanical strength.

REFERENCES

1. Z. H. Qiao, D. M. Jie, H. M. Liu, Y. Ge and H. Y. Zhang, "Extraction of water-soluble polysaccharide and the antioxidant activity from Ginkgo biloba leaves", *Med Chem Res*, vol. 19, pp. 262-270, 2022.
2. H. E. Seifried, "Oxidative stress and antioxidants: A link to disease and prevention?", *J Nutr Biochem*, vol. 18, pp. 168-171, 2020.
3. J. Sun, J. Y. Yao, S. X. Huang, X. Long, J. B. Wang and E. Garcia-Garcia, "Antioxidant activity of polyphenol and anthocyanin extracts from fruits of Kadsura coccinea (Lem.) A.C. Smith", *Food Chem*, vol. 117, pp. 276-281, 2019.

4. H. Wang, V. E. C. Ooi and P. O. Ang, "Anti-herpesviral property and mode of action of a polysaccharide from brown seaweed (Hydroclathrus clathratus)", *World J Microbiol Biotechnol*, vol. 26, pp. 1703-1713, 2018.
5. Ismail and T. S. Hong, "Antioxidant activity of selected commercial seaweeds", *Mila J Nutr*, vol. 8, pp. 167-177, 2010.
6. K. S. Kumar, K. Ganesan and P. V. S. Rao, "Antioxidant potential of solvent extracts of Kappaphycus alvarezii (Doty) Doty − An edible seaweed", *Food Chem*, vol. 107, pp. 289-295, 2008.
7. P. Matanjun, S. Mohamed, N. M. Mustapha, K. Muhammad and C. H. Ming, "Antioxidant activities and phenolics content of eight species of seaweeds from north Borneo", *J Appl Phycol*, vol. 20, pp. 367-373, 2008.
8. M. C. Rocha de Souza, C. T. Marques, C. M. Guerra Dore, F. R. Ferreira da Silva, H. A. Oliveira Rocha and E. L. Leite, "Antioxidant activities of sulfated polysaccharides from brown and red seaweeds", *J Appl Phycol*, vol. 19, pp. 153-160, 2007.
9. Y. V. Yuan, D. E. Bone and M. F. Carrington, "Antioxidant activity of dulse (Palmaria palmata) extract evaluated in vitro", *Food Chem*, vol. 91, pp. 485-494, 2005.
10. Q. Zhang, P. Yu, Z. Li, H. Zhang, Z. Xu and P. Li, "Antioxidant activities of sulfated polysaccharide fractions from Porphyra haitanesis", *J Appl Phycol*, vol. 15, pp. 305-310, 2003.
11. Y. F. Yang, J. Q. Feng, H. Y. Xu, D. M. Peng and J. P. Hu, "Influence of Different Extraction and Purification Methods on Astragalus Polysaccharides and Pharmacological Evaluation", *Chin Herb Med*, vol. 2, no. 1, pp. 54-61, 2010.
12. B. Wang, C. G. Yu, H. Y. Luo, Y. L. Qu and L.Y. Yang, "Studies on the Preparation and Antioxidant Properties of Enzymatic Hydrolysate from Dasyatis akajei by Papain [J]", *Food Sci Technol Int Food*, vol. 10, no. 4, pp. 113-118, 2010.
13. Cheng and W. Li, "Antioxidant activity of water soluble polysaccharide from several plants", *Sci Technol Food Ind J*, vol. 27, pp. 63-65, 2006.