

Synthesis and testing for mechanical integrity of nano cellulose composites

This scientific research focused on extraction of the polymer from an appropriate source and preparation of films with mechanical integrity and desirable chemical properties. Reinforcement of said films with nano-fillers like Nano silica and clay were administered to reinforce their mechanical properties. Further development on these films would contribute to eliminating plastics and replacing them with better and sustainable materials. Cellulose may be a biopolymer found in plant cell walls which will be derived from biomass sources like sugarcane. It is one among the main constituents of plant cell walls alongside hemicellulose and lignin. "Cellulose consists of long unbranched fibers of glucose held together by hydrogen bonds". It is widely utilized in paper, plastics, coatings and casings.

Keywords: Cellulose, hemicellulose, biopolymers, reinforced films, biodegradable.

1.0 Introduction

The plastic waste disposed of by human beings is next to impossible to decompose. The pollution of land and water bodies is a cause of panic and concern throughout the world in recent years. Pollution not only affects climate change, which is another major concern, but also harms animals and plant life to a large extent. The prime source of this widespread pollution is plastic. These catastrophic problems, which are the effect of human caused pollution of land and water bodies, are the major factors forcing industries to look for alternatives to plastics and plastic products worldwide. Over the years many methods have been incorporated to deal with the overuse of plastic; like reusing plastic products for other purposes, and recycling. Many countries have adopted laws banning the use of plastic covers and packaging. They are instead, encouraging the use of cloth bags or biodegradable plastic covers.

A biopolymer is a polymeric biomolecule produced by living organisms. It contains monomeric units that are

covalently bonded to form larger structures or molecules. The name "Biopolymer" implies that it is a biodegradable polymer. "Cellulose is the most common organic compound and biopolymer on Earth. About 30-60 per cent of all plant matter is cellulose". It is found in the plant cell walls alongside two other biopolymers namely: hemicellulose and lignin.

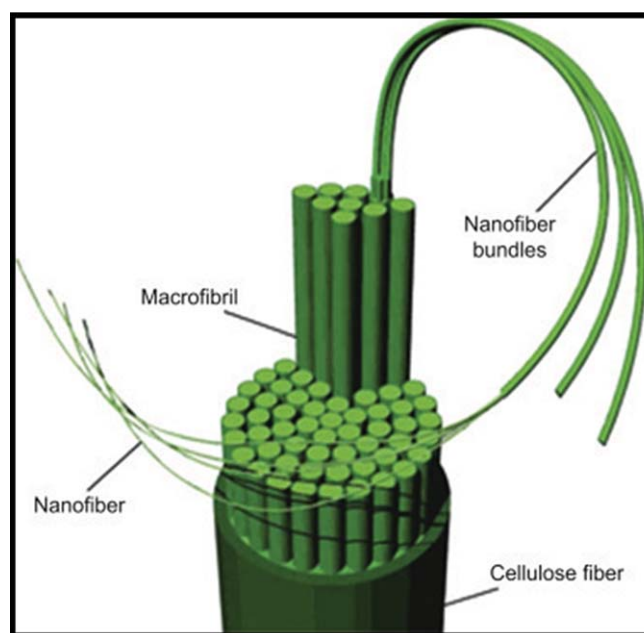


Fig.1: Structure of cellulose

1.1 EXTRACTION OF POLYMERS FROM BIOMASS

Chemical processes can be used to effectively separate the three constituents: cellulose, hemicellulose and lignin. The most commonly used extraction method to remove hemicellulose and lignin from the biomass is the alkaline extraction method. In this method, the SCB is soaked in a solution of 0.5M NaOH and stirred continuously for 3-4 hours at 60°C. The solution is then filtered through a fine filter paper. The filtrate contains hemicellulose and lignin while the residue is rich in cellulose. This method is normally done to remove hemicellulose from the biomass. The hemicellulose yield obtained from this is around 40-75% of the original biomass Which in turn implies that the cellulose left behind is almost pure. According to Loh et al., "Sodium hydroxide (NaOH)

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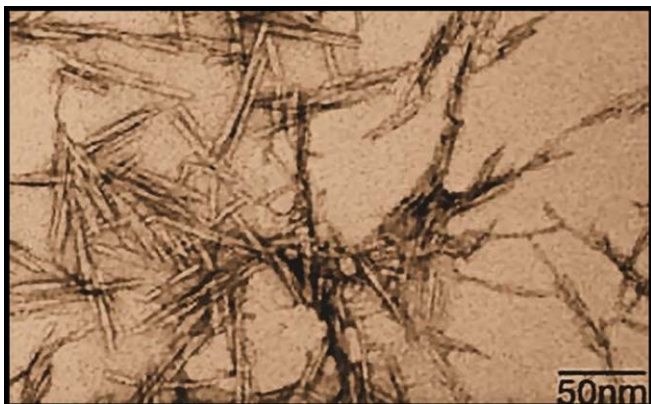


Fig.2: Micrograph of randomly oriented Nano cellulose

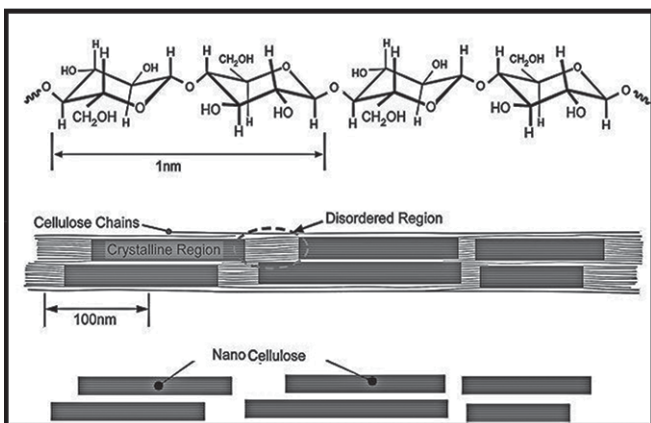


Fig.3: The first figure shows the structure of cellulose polymer; the second figure shows nano fibrils with crystalline and amorphous cellulose; the third figure shows cellulose nanocrystals after amorphous cellulose is removed by acid hydrolysis

extraction will yield 56.1% cellulose, 8.8% hemicellulose and 4.9% lignin while sulfuric acid (H_2SO_4) will yield 63.6% cellulose, 0% hemicellulose and 22.5% lignin". FTIR analysis of CNC showed that the characteristic peaks of hemicellulose and lignin were absent due to complete removal via acid hydrolysis.

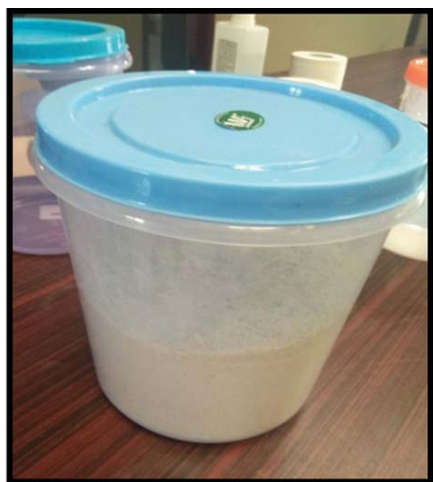


Fig.4: Ground SCB



Fig.5: Acetylation using buffer solution



Fig.6: Vacuum assisted filtration

1.2 ACID HYDROLYSIS

Acid hydrolysis is a chemical step that is used to break chemical bonds via a nucleophilic chemical reaction. This step is thus being crucial in obtaining cellulose fibers as nanocrystals.

After hemicellulose has been separated from the SCB, the remaining portion of the SCB is soaked in an acid solution of H_2SO_4 of 60% concentration and spun for 5 hours at $45^\circ C$. After hydrolysis is completed, the acid solution is centrifuged for 15 minutes at 4000 rpm. The SCB and Nano cellulose are separated at this stage due to their molecular weights. The nano cellulose is deposited on top of the heavier SCB particles and is to be scooped out and suspended in DI water and stored in a fridge.

1.3 REINFORCEMENT

There is a need to provide reinforcement to the cellulosic films in order to fill the voids and enhance the overall strength of the films. "Nano-fillers with high aspect ratio have higher specific surface area, providing better reinforcing and bonding effects and lead to marked improvement in properties when compared to pure polymers or their traditional composites. Properly chosen polymer matrix and filler particles will give polymer composites having much better polymer-filler interactions than conventional composites" [3].

Nano cellulose was extracted from readily available plant biomass, sugarcane bagasse, for making biodegradable plastics, films for packaging and used in other applications such as edible coatings, pharmaceutical industries, etc. The biomass from SCB cannot be directly used for making films with desired mechanical properties as it initially contains lignin, a highly rigid material. Hence, in the present investigation, the cellulose which forms 40-50% of the bagasse and hemicellulose which forms 20-25% is extracted from the sugarcane bagasse, using methods like alkaline extraction, chlorite pre-treatment, acid hydrolysis. However,



Fig.7: Nano cellulose



Fig.8: Nano cellulose + PVA and nano cellulose + PVA + 1 wt% nano-silica



the nano cellulose alone cannot be used to make packaging films due to its brittle nature and low tensile strength. Hence, it is to be blended with other composite polymers such as polyvinyl alcohol (PVA). These composite cellulose films have potential to perform as efficient packaging films.

2.0 Methodology

The SCB of about 5-6 kg was collected, washed and dried in hot air oven at 60°C for 48 hours.

The dried bagasse was then dewaxed using cyclohexane for 2-3hrs. It was then ground into fine dust.

A buffer solution of 500 mL was prepared in a conical flask using acetic acid and sodium acetate with a pH of 4.6. To this 10g of SCB dust was added and stirred for an hour at 80°C. This ensures the partial delignification of the SCB biomass.

5g of sodium chlorite (NaClO_2) was added to the flask and this was further stirred for 3 hours. This was done to bleach the SCB so as to obtain nearly transparent films. There was a noticeable colour change from white to yellow after a couple of hours indicating the bleaching was completed.

The base matrix of each of the composite films was made of PVA or polyvinyl alcohol which was used as the binding agent; and the nano cellulose extracted from SCB. After the films were mixed with the reinforcing material, according to weight, they were poured onto a flat hot pan at 60°C. Since the films are made up of thermoplastic polymer PVA, temperature was maintained constant throughout the drying process.

- In order to make the film, a 150 mL beaker is washed and dried.
- Appropriate amounts of nano cellulose that is squeezed, dried and PVA are added to get a total solid weight of 10gms.
- About 120 mL of DMSO is added and the mixture is stirred at 60°C until the nano cellulose and PVA has completely dissolved in the DMSO.
- This solution is then poured onto a nonstick pan and

allowed to dry at 50°C. This process may take up to 2 days.

The average thickness of the film was measured using Oxford digital screw gauge and was determined to be 140 microns (0.14mm).

Reinforcement

Nano-silica extracted from another organic waste, rice husk; and clay nano-platelets were used as composite additives to modify the properties of the film on a nano scale. Both reinforcements are biodegradable.

- Rice husk was obtained from local organic store and was heated in furnace from 100-800°C at the rate of 50°C/15 min. The rice husk ash that is obtained contains 97% silica.
- 10g of rice husk ash is then heated and stirred for 3 hrs in 100 mL of 2.5 N sodium hydroxide (NaOH). Filtered residue is washed with 40 mL of distilled H_2O (boiling). The transparent filtrate obtained was then cooled to room temperature.

With nano cellulose, PVA and dimethyl sulphoxide (DMSO) making up the base matrix, varying amounts of nano-silica based on weight were added as reinforcement to the film.



Fig.9: Rice husk ash



Fig.10: Nano-silica

- The nano-silica was weighed accordingly and added to about 80 mL of DMSO in beaker. The beaker along with its constituents was placed in an ultrasonic bath sonicator, to disperse the nano-silica evenly in the DMSO solvent, for about 10-15 minutes.
- The nano cellulose and PVA are then added to the beaker and stirred, using a magnetic stirrer for 3 hours at 50-55°C. Once it is completely mixed, the film is poured onto a pan and left to set at 60°C.

Nano cellulose film microstructure images are taken with the help of scanning electron microscope.

3.0 Results and discussion

The tensile test data were recorded using micro UTM (Mecmesin) with test load of 50N and 1 mm/min extension (sample dimension 4×1 cm²).

The tensile strength of the film compared to the nano cellulose, PVA added NC exhibits good strength values. Of the composite films, there is a margin of improvement



Fig.11: Nano cellulose + PVA+ 1 wt.% clay



Fig.12: Nano cellulose + PVA + 2.5 wt % clay

obtained through the silica particle reinforcement in the film, which exhibit reduced free volume in the polymer and offers hydrogen bonding enhancement for strength.

A 2.5 wt.% loaded silica particle in the film makes the film stiff by a 4 times increase in the matrix values compared to the neat NC alone. Hence, it is inferred from the data, that the addition of silica particles at a optimized level could potentially enhance the matrix strength which could be a desirable property of degradable materials applicable for commercial packaging application.

The clay loaded films with 4 wt.% show good retention property after aging too, similar to a 2.5 wt% silica loaded film of both UTS and YM.

3.1 TENSILE STRENGTH

The tensile strength of the film shows in Fig.15, compared to the nano-cellulose, PVA added NC exhibits good strength values. Of the composite films, there is a margin of improvement obtained through the silica particle reinforcement in the film, which exhibits reduced free volume in the polymer and offers hydrogen bonding enhancement for strength

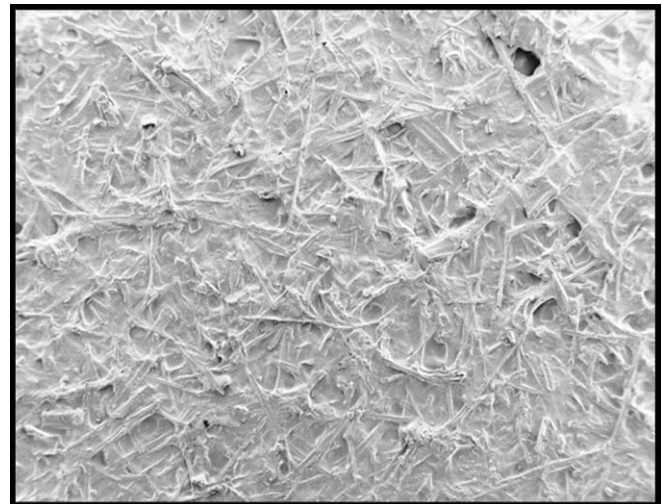


Fig.13: SEM picture of 100% nano cellulose film

A high loading of silica particle in the film exhibit slight reduction in the film strength but better than the unreinforced film. This effect could be due to the possible agglomeration of silica particles surfaces within them in the film. So, a proper and optimized loading of the silica particle reinforcement might give good film strength without compromising the other essential properties of the film. A similar effect also observed in the clay loaded films

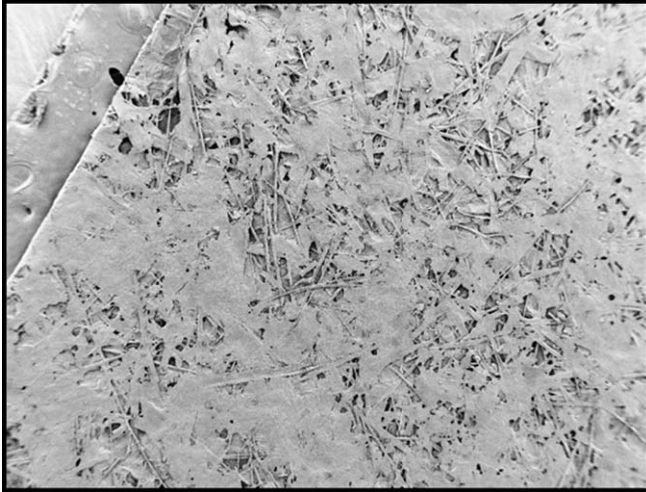


Fig.14: SEM picture of nano cellulose with PVA

3.2 YOUNG'S MODULUS

The Young's modulus, a measure of matrix toughness, shows a similar trend to that of tensile strength. A 2.5 wt% loaded silica particle in the film makes the film stiff by a 4 times increase in the matrix values compared to the neat NC alone. Hence, it is inferred from the data, that the addition of silica particles at an optimized level could potentially enhance the matrix strength which could be a desirable property of degradable materials applicable for commercial packaging application.

FTIR spectra analysis of individual peaks

1. Peak identification and baseline correction of the peaks.
2. Gaussian curve fitting were followed on the second derivative of the peaks of interest.
3. Full width half maximum (FWHM) analysis of the

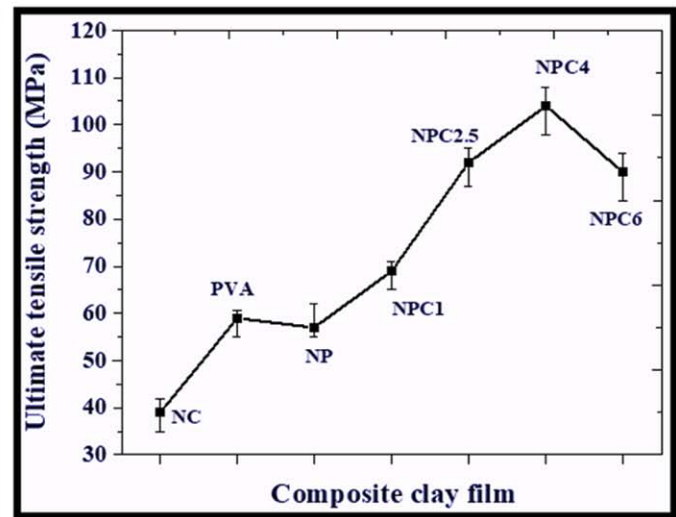
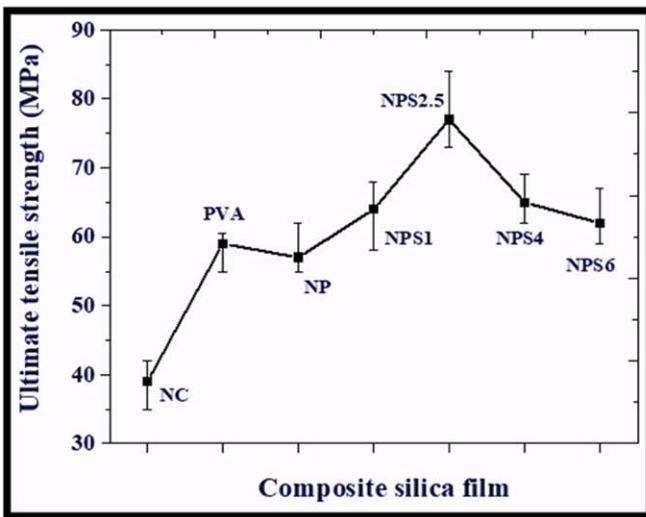


Fig.15: Ultimate tensile strength of composite silica film and clay film respectively

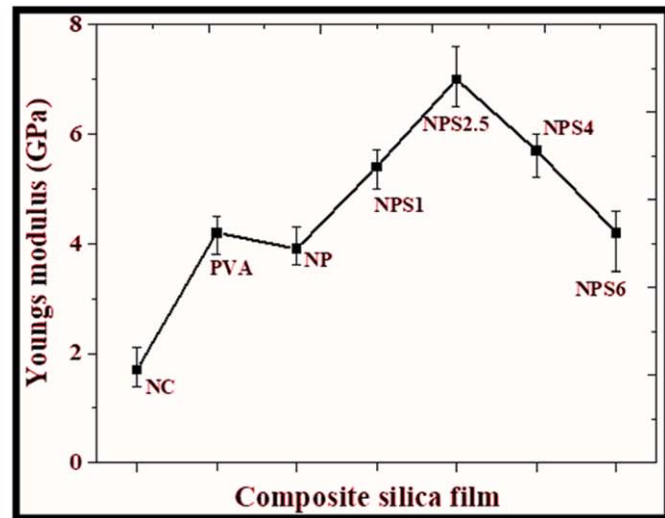
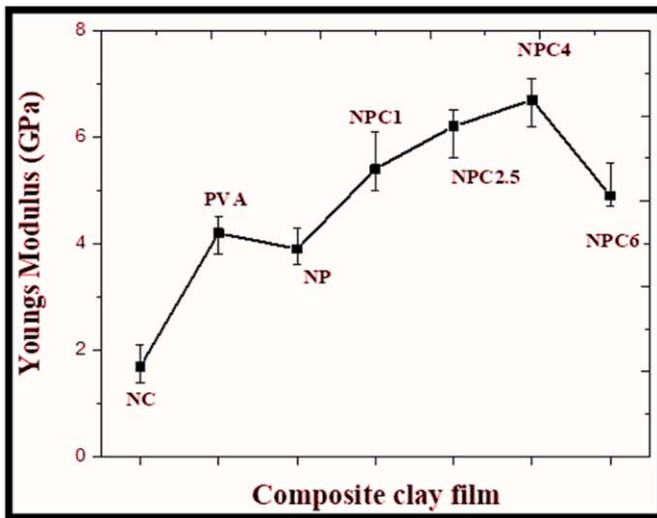


Fig.16: Young's Modulus of composite clay film and silica film respectively

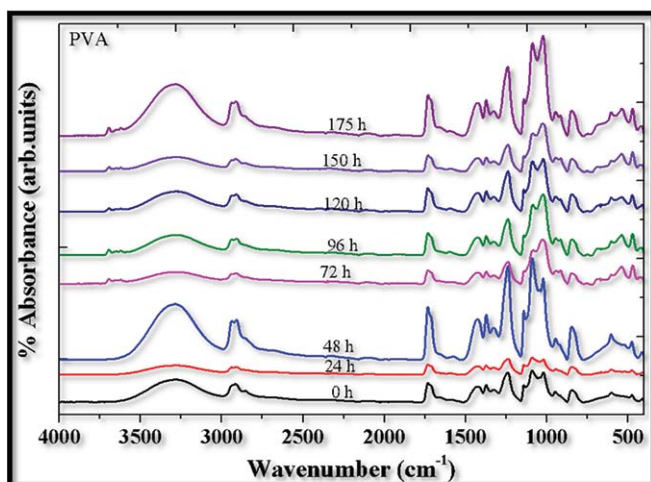
particular peak were performed while taking ratio for comparison.

Full width half maximum (FWHM) analysis of the particular peak were performed while taking ratio for comparison.

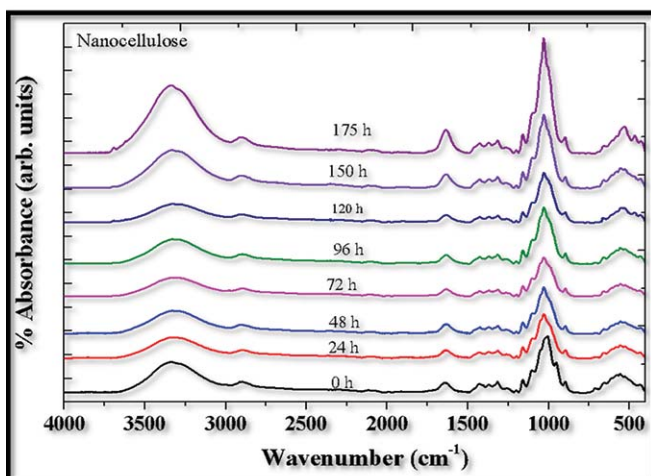
3.3. COMPARISON

“The isolated Nano cellulose from sugarcane bagasse shows the basic structural features of cellulose I profile denoted by intramolecular hydrogen bonding between various types of –OH groups in cellulose materials ranging from 3600-3100 cm^{-1} . The peak intensity of the hydrogen bonds from the spectra of celluloses becomes wider and with lower intensity, when the aging time increases.

There is a strong broad band at around 3400 cm^{-1} , which is assigned to different O–H stretching modes, and another two bands at around 2920 and 2850 cm^{-1} , related to asymmetric and symmetric methyl and methylene stretching groups present in the spectra of all of the sample components”. [5]



(a) Absorption spectrum of nano cellulose



(b) Absorption spectrum of PVA

Fig.17: Absorption spectrum of Nano cellulose with PVA contains 1% silica

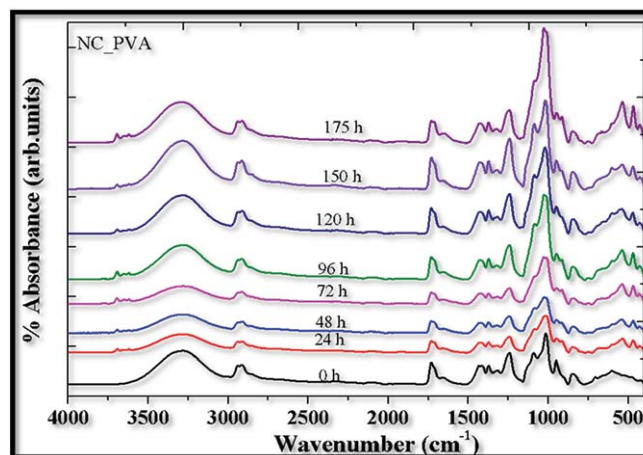


Fig.18: Absorption spectrum of Nano cellulose with PVA contains 1% silica

4.0 Conclusions

Studies on cellulose: Nano cellulose, and hemicellulose composites with a variety natural fibers as reinforcement, which are also available as bio wastes, can lead to synthesis of materials that have good mechanical properties such as tensile strength and elasticity are enough to replace plastics. Addition of silica particles at an optimized level could potentially enhance the matrix strength. For food-grade usage regarding safety and stability with exposure to moisture and heat might reveal more useful properties that lead to very specific eco-friendly applications in food packaging.

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