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Extraction, Characterization and Evaluation of Reinforcing Nanocellulose in Polyvinyl Alcohol (PVA)

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This is to certify that the thesis prepared by Teshale Tadesse entitled: ***Extraction, Characterization and Evaluation of Reinforcing Nanocellulose in Polyvinyl Alcohol (PVA)*** and submitted in partial fulfillment of the requirements for the degree of Master of Sciences (Chemical and Bio Engineering) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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Lists of Abbrevations

PVA	Poly (vinyl alcohol)
DLS	Dynamic light scattering
FTIR	Fourier transfor inrared spectroscopy
SEM	Scanning electron microscopy
NC	Nanocellulose
B	Sugarcane bagasse
C	Cellulose
PVA/0%NC	Poly (vinyl alcohol) reinforced with 0 % wt. nanocellulose suspension
PVA/3%NC	Poly (vinyl alcohol) reinforced with 3 % wt. nanocellulose suspension
PVA/5%NC	Poly (vinyl alcohol) reinforced with 5 % wt. nanocellulose suspension
PVA/7%NC	Poly (vinyl alcohol) reinforced with 7 % wt. nanocellulose suspension
PVA/5%B	Poly (vinyl alcohol) reinforced with 5 % wt. grounded bagasse suspension
PVA/5%C	Poly (vinyl alcohol) reinforced with 5 % wt. cellulose suspension
Neat PVA	Poly (vinyl alcohol) reinforced with 0 % wt. nanocellulose suspension
PDI	Polydispersibility index

Abstract

Incorporating nanocellulose into different materials have become an attractive research topics for production of nanocomposite materials. The objective of this study was to extract nanocellulose from the bagasse and apply as reinforcement in the PVA polymer, and evaluate the effectiveness of the reinforcement. The extraction of nanocellulose was performed by acid hydrolysis with 50 % wt. H_2SO_4 at 45°C for 45 minutes and 40 % yield was obtained. The particle size analysis by dynamic light scattering (DLS) showed the mean particle size found was 348.6 nm, confirming the product was nanocellulose. The Fourier transform infrared spectroscopy (FTIR) indicated the effectiveness of pretreatment in removing lignin and hemicellulose. The nanocellulose was reinforced in PVA polymer by solvent casting process. The water absorption results revealed that reduction in percentage of water absorption from 82 % for neat PVA to 59 % PVA/ 7 %NC. This results were confirmed by increment in tensile strength from 33 MPa for neat PVA to 53 MPa for PVA/ 5 %NC and reduction in elongation at break about 2.4 folds with respect to neat PVA. The SEM micrograph showed uniform distribution and formation of network structure through hydrogen bonding. The comparative and cluster analysis showed the nanocellulose reinforced PVA films exhibited highest tensile strength, lower elongation at break and lower water absorption with respect to bagasse and cellulose reinforced PVA as well as with neat PVA film.

1. Introduction

1.1. Background

Among agro-industrial residues, sugarcane bagasse is lignocellulosic biomass produced in in large quantities by the sugar and alcohol industries [1]. In spite of huge production, majority of this bagasse have been not utilized and menace to environment. For example, Pandey and Soccol have reported that about 50% of produced bagasse has mainly been utilized for generating steam and electricity within plant as a fuel source and remaining unused bagasse is usually disposed to environment that causes environmental problem [2]. Thus, several processes and products have been reported to utilize this bagasse as a raw material for processing bio-based chemical and products such as charcoal, briquettes, pulp and paper, cardboard, fiber board, activated carbon, furfural, alpha-cellulose, xylitol and polymers [3].

In the case of Ethiopia, for the last decades, the Ethiopian government has made significant investments in order to boost the production capacity of sugar. According to the Ethiopia Sugar Corporation, the expected sugar production plan is 4.2 million metric tons by 2023 and the plan is to make the country one of the top ten world's largest sugar producers [4]. These efforts have and will continue not only increase production capacity of sugar but also increase the amount of bagasse residues **.**This will also increase generation of the bagasse than current production capacity in the same rate. For example, according to the UN report, between academic year of 2010 and 2013, Ethiopia produced about 4108 thousand metric tons of bagasse [5]. In spite of being good increasing the production capacity, this brings some environmental inconvenience, such as the generation of a huge amount of bagasse. Every metric ton of sugarcane generates about 280 kg of bagasse [6]. Some of this bagasse is utilized for generating steam and electricity within plant and remaining huge amount of bagasse is still not used [2].

Since bagasse is composed mainly by cellulose (30–50%), many papers have been published aiming at the utilization of bagasse cellulose for production of several cellulose derivatives such as nanocellulose for different applications. Nanocellulose is produced by strong acid hydrolysis treatment such as sulfuric acid, in which the amorphous regions in cellulose are more accessible to acid and more susceptible to hydrolytic action than the crystalline region and remove the amorphous regions [7, 8].

For this reason, incorporating nanocelulose into different materials has become an attractive alternative research topic for production of nanocomposites to replace synthetic petroleum based polymers. Thus, many researchers have been conducting an experiment on reinforcement of polymer with nanocellulose materials due to its specific properties related to their lower density, renewability, high strength, biodegradability, transparency and other properties which cannot achieved in with other materials [9-11]. Among these polymers, PVA has been widely used in research studies for preparation of blends and composites like chitosan, nanocellulose, starch or lignocellulosic fillers [12]. This arise from its desired natural characteristics such as being able to chemically bond with cellulose, soluble in water , easy to process, biodegradable, biocompatible, non-toxic, easily to form and hydrophilic properties [13].

Therefore, due to its good source of cellulosic fibres, it is important to convert this unused bagasse residues into value-added such as nanocellulose products along with the utilization for the production of fuel, chemicals, pulp and papers. Hence, this research paper was selected to extract nanocellulose from sugarcane bagasse and reinforced in polymer for the purpose of studying its effectiveness on poly (vinyl alcohol) (PVA) polymer. The aim was to produce nanocellulose from sugarcane bagasse and to convert unused bagasse generated from Ethiopian sugar industries into value added product as an alternative option minimizing environment problem. Moreover, the application of nanocellulose in composite materials have been gaining a lot of attention because of its nano dimension, biodegradability, abundance, high strength, renewability and uniform dispersion in matrix makes a good candidate for the preparation of polymer nanocomposites and open a wide range of possible discoveries.

1.2. Statement of the problem

The reduction of petroleum resources and rising petroleum costs, there is concern with finding cost-effective ways to manufacture different materials from renewable and abundant natural resource. A viable solution to overcome these diminishing petroleum resources coupled with global environmental problem is extract nanocelulose from agricultural wastes such as sugarcane bagasse and incorporate in polymer matrix for production of composite materials for our daily usage. Not only this but also most of polymer products are largely discard into environment upon usage and are not easily biodegradable. As result, they are leading to serious environmental problem that affects our environment and societies. The alternative option for such problem is to produce biodegradable composites based on natural resources such as nanocellulose derived from agro-wastes such as bagasse. Therefore, it was important to extract nanocellulose from bagasse and investigate the effect of reinforcing the nanocellulose in polymers.

While much recent outstanding progress has been achieved in nanocellulose production and reinforcing in polymeric materials, there are many challenges remaining in terms of efficiency and economical production to be used as reinforcement. Hence, it was important to investigate the efficiency and effectiveness dispersion of nanocellulose in polymeric matrix. Several studies reported on the dispersion of nanoscale size fillers and nanofibers such as nanofillers such as nanosilicon dioxide, nanoclays, cellulose and micro cellulose into polymer to improve their properties. However, these had little influence on properties and uniform dispersion in the polymer matrix.

To overcome these limitations and environmental problem concerning polymer products, this paper was selected to extract nanocellulose from bagasse and reinforced in PVA polymer to evaluate its effectiveness of the reinforcement. Additionally, large generation of unused bagasse from sugar industries in Ethiopia and its high cellulose content have attracted this research topic to produce value added nanocellulose product for composite production. Moreover, the usage of nanocellulose have been gaining a lot of attention for the preparation of polymer nanocomposites and open a wide range of possible discoveries because of its nano dimension, biodegradability , abundance, high strength , renewability and uniform dispersion in matrix

1.3. Objective of the study

1.3.1. General objective

The general objective of this thesis was to extract nanocellulose from sugarcane bagasse and reinforce in poly (vinyl alcohol) (PVA) polymer matrix.

The aim of the research was to extract nanocellulose from sugarcane bagasse agro- waste and apply as reinforcement to polyvinyl alcohol (PVA) polymer matrix, and evaluate the effectiveness of the reinforcement.

1.3.2. Specific objectives

The specific objective of the research was:

- To extract and prepare nanocellulose from sugarcane bagasse by acidic hydrolysis
- To characterize the nanocellulose using dynamic light scattering (DLS) and Fourier transform infrared (FTIR) spectroscopy
- To produce PVA-nanocellulose composite films using solvent casting
- To characterize the reinforced composite films
- To evaluate effectiveness of the reinforcement by using water absorption test, FTIR, scanning electron microscopy (SEM) and mechanical test
- To compare and evaluate the reinforcement with neat PVA, with bagasse and cellulose reinforced PVA.

1.4. Significance of the study

The significance of extracting and reinforcing nanocellulose in polymer matrix was to utilize sugarcane bagasse agro-wastes for production of nanocellulose for various applications such as for reinforcement in polymeric, biomedical and other applications. This provides composite materials that can be degraded and improved properties that plays vital role in the variety of application for their outstanding performance. The demands of polymeric materials are increasing rapidly for different applications such as packaging, building and construction, aeronautics, medical and automotive devices. But, most of these products are not environmentally friendly and not easily biodegradable upon discard to the environment causing serious environmental. However, there is an alternative option such as production and application of biodegradable composites based on natural resources derived from agro-wastes that provide environmental benefits.

The reduction of petroleum resources and rising its cost, there is concern with finding cost-effective ways to produce different materials from renewable and abundant natural resource. By using renewable and abundant natural resource such as bagasse for production of composite materials, nanocellulose can provides a viable solution to overcome the issues concerning diminishing petroleum resources coupled with global environmental problem.

The other advantage of this investigation was to provide a way of converting unused agro-waste sugarcane bagasse residues into value added product such as nanocellulose for composite production. By 2023, Ethiopia Sugar Corporation´s plan is to make the country one of the top ten world's largest sugar producers with production capacity estimated about 4.2 million metric tons which also increase generation of bagasse than current production capacity [4]. Currently, however, most of bagasse was remain unused; it was disposed to environment or burned either onsite or offsite that significantly contribute to ward environmental pollution.

Apart from these, the investigation of this research was important to provide the opportunity for nano - engineered biomaterials in composite processing that opens new area of research in Ethiopia for converting unused bagasse into nanocellulose.

2. Literature Review

2.1. Sugarcane Bagasse

In recent years, the utilization of renewable resources such as sugarcane bagasse has been increasing for industrial application to produce different bio-based products. Sugar bagasse is lignocellulosic residue produced in in large quantities by sugar and alcohol industries [1]. Annually, about 5.4 x 10^8 dry ton of sugarcane processed to extract sugar juice and every metric ton of sugarcane generates about 280 kg of bagasse [6]. Inspire of huge production, majority of this bagasse have been not utilized and menace to environment. For example, Pandey and Soccol reported that about 50% of produced bagasse has mainly been utilized for generating steam and electricity within plant as a fuel source and remaining unused bagasse is usually discarded or stockpiled to environment that causes environmental problem [2].

Thus, several processes and products have been reported in order to utilize this bagasse as a raw material for processing bio- based chemical and products. For instance, Oliver D. Cheesman has described excellent utilization of bagasse as raw material for production various products such as charcoal , briquettes , pulp and paper , cardboard, fiber board, activated carbon, furfural, alpha-cellulose, xylitol and polymers [3]. Bagasse contains 40-50 % cellulose, 23- 35 % hemicelluloses and 15–35% lignin with other impurities [7, 8]. This high content of cellulose is an excellent sources of cellulose fibers for the extraction of cellulose derivatives. One of the most important cellulose derivatives is nanocellulose, which is widely used in several application such as in production of bio-composite products. Thus, many researchers have been attracted toward utilization of sugarcane bagasse for extraction of nanocellulose as potential resources in developing new materials and products [3].

Therefore, suitable utilization of this bagasse being an important objective to convert this waste into value-added products along with the utilization for the production of fuel, chemicals, pulp and papers . It is a good source of cellulose fibres which can be converted into nanocellulose. The importance of extracting nanocellulose from these bagasse reinforcing in polymeric matrix and other application due to its biodegradability, renewability, high specific surface area, high specific strength and stiffness [7, 8].

2.2. Challenges and perspectives of bagasse in Ethiopia

In last decades, the government of Ethiopia has made significant investments in order to boost the production capacity of sugar. According to the Ethiopia Sugar Corporation, by 2023, the plan is to make the country one of the top ten world's largest sugar producers with production capacity estimated about 4.2 million metric tons [4]. This plan will also increase generation of sugarcane bagasse (SCB) than current production capacity. For example, according to the UN report, between academic year of 2010 and 2013, Ethiopia produced about 4108 thousand metric tons of bagasse [5]. The Ethiopia Sugar Corporation has made heavy investments on sugar sector to construct new sugar processing factories, to renew older factories, and to expand land for sugarcane cultivation [4]. These efforts have and will continue not only increase production capacity of sugar but also increase the amount of bagasse residues. Abundance of this cellulosic material in Ethiopia can be readily to provide a new research area for extraction and application of various bio-products such as bio-composite polymers.

In order to utilize this unused bagasse as a raw material, several method of utilization has been reported. These include electricity generation, pulp and paper production, and products based on fermentation [20]. Therefore, conversion of leftover bagasse into value-added products have sustainable economic and strategic benefits along with the utilization for the production of fuel, chemicals, papers, newspapers, etc. is challenging issue [21, 22].

Therefore, this thesis proposed to provides a new area for research development in Ethiopia in which the bagasse can be converted to nanocellulose and used for different application including reinforcing in polymer matrix that can address issues regarding bagasse. Due to its superior characteristics such as nanoscale dimension, high surface area, high availability, high crystalline, stiffness, biodegradability and renewability, it has been used for different application including in construction, packaging, automobile, transportation, and biomedical fields [22, 23]. This conversion into value added product is not only produce nanocellulose but also change negative cost of the bagasse into positive- earning materials by minimizing environmental problem and fossil fuel dependence of polymeric material [22].

2.3. Bagasse for reinforcement in polymeric matrix

Over the last few years, utilization of sugarcane bagasse as reinforcement in polymeric matrix is increase rapidly. Several research reports have been published on the application of sugarcane bagasse as reinforcement in polymeric matrix [24]. For instance, R.Dugnani et al. has reported excellent review on the agricultural waste fibers toward sustainable utilization and concluded that cellulosic fibers were being used as potential reinforcing materials for production of agro-based bio – composite [25].

Also the potential of sugarcane bagasse as reinforcement in polymeric matrix were published by different reports [29]. Dhaiwat Trivedi and Nikunj Rachchh have presented review on bagasse fiber reinforced polymer composite and reported that bagasse fiber composites have achieved good mechanical properties [28]. The papers concluded that the usage of sugarcane bagasse as reinforcement in polymer matrix for composite production seems to be bright because of their superior properties, its cheapness, and lightness in weight, renewable and easily available. Another study reviewed the usage of sugarcane bagasse in composite material and reported that the bagasse and its derivatives can be utilized and applied for composite material production for various applications [27].

Moreover other several studies have reported that bagasse and its derives can be utilized and applied for reinforcement in different polymeric materials such as reinforcement in low density Polyethylene LDPE), bagasse reinforced polypropylene Composite, sugarcane nanocellulose poly (vinyl alcohol) composite, polystyrene (PS) reinforced with residues of sugarcane natural fibers , sugarcane bagasse fiber Polyvinyl chloride (PVC) composite [27].

2.4. Challenges and future trends of nanocellulose for nanocomposites

Due to changing consumer perceptions, increasing ecological considerations, and technological advances, recent development in sourcing materials from renewable natural resources are likely to continue [13,16-19].This also increased from nanocellulose and composites viewpoint, nanocellulose offer an interesting application for polymer matrices, additives and reinforcement for production of different composite materials [9-11, 13]. This nanocellulose offer potential benefits in specific properties related to their lower density, renewability, high strength, biodegradability, transparency and other properties which cannot achieved in with other materials.

However, the use of nanocellulose as reinforcement for production of different composite materials is at young stage [15]. Nanocellulose reinforcing potential has not yet fully realized because of issues related to scaling up into industrial manufacturing processes. This is due to insignificant quantities of nanocellulose are available to use for wide-scale research, industrial manufacturing processes and development efforts [9-10]. Recently, recent pilot- and plant-scale nanocellulose production was reported at commercial and government level that will likely improve the situation [10, 11]. Therefore, production of nanocellulose has attracted attentions of several researchers for composite material production.

While much recent outstanding progress has been achieved in nanocellulose production and reinforcing in polymeric materials, there are many challenges remaining in terms of efficiency and economical production to be used as reinforcement [9, 10]. Hence, more efficient and effective methodology need to be found for producing nanocellulose with optimal characteristics that will require additional research to address the issues related to their hydrophilic nature for widespread application [13, 15].

For further appropriate applications, adequately dispersion of nanocellulose as reinforcement into a variety of matrices are needed to be identified, investigated, demonstrated , understood and addressed for incorporated into different materials. There are several studies reported on the dispersion of nanoscale size fillers and nanofibers into polymer such as PVA in order to improve their properties [16-19]. Most of these studies used nanofillers such as nanosilicon dioxide, montmorillonite clay, sodium montmorillonite clay and nanoparticles of poly (methyl methacrylate-co-acrylamide), cellulose and micro cellulose [11, 16-19].

However, these nanoparticles and cellulose had little influence on mechanical and physical properties such as biodegradability properties, uniform dispersion in the polymer matrix [15].

To overcome these limitations, this research paper was selected to extract nanocellulose from sugarcane bagasse and reinforced in polymer for the purpose of improving the properties of PVA reinforced with the nanocellulose. Additionally, large generation of unused sugarcane bagasse from sugar industries in Ethiopia that dispose to environment have attracted this thesis to convert this unused lignocellulosic material into value added product. This large generation of bagasse and its high cellulose content have attracted have motivated this research to produce nanocellulose for use as a reinforcement in composites materials. Moreover, the usage of nanocellulose have been gaining a lot of attention because of its nano dimension, biodegradability , abundance, high strength, renewability and uniform dispersion in matrix makes a good candidate for the preparation of polymer nanocomposites and open a wide range of possible discoveries .

2.5. Nanocellulose reinforcement in PVA

The use of nanocelulose derived from renewable biomass resources as a reinforcing phase in polymeric matrix provides positive benefits in terms of biodegradability, high mechanical properties, inexpensive, renewable, low density and environmental benefits with respect to ultimate disposability and raw material usage [27]. Many reports have shown considerable interest for the extraction and incorporation of nanocellulose as reinforcement in various polymers such as poly (vinyl alcohol) (PVA), polyurethane, polypropylene poly (lactic acid) (PLA) and polyacrylamide [30-34].

Among these polymers, PVA is hydrophilic synthetic polymers that have desired characteristics desired for different applications such as being easy to process, biodegradable, biocompatible, non-toxic, easily to form and hydrophilic properties [12]. Being able to chemically bond with cellulose and soluble in water, PVA has been widely used for the preparation of blends and composites with several natural, renewable polymers like chitosan, nanocellulose, starch or lignocellulosic fillers.

Because of these interesting properties, PVA has been the subject of composite research field. For instance, M. J. Cho and B. D. Park investigated the mechanical and thermal properties of PVA-based nanocomposites reinforced with nanocellulose and showed that the tensile modulus increased with an increase of nanocellulose loading [35]. Similarly, nanocellulose reinforcement in PVA has improved its mechanical and thermal properties. For example, Paiva et al**.** and S. Virtanen et al. prepared PVA nanocellulose composites through solvent casting and found that the mechanical properties of the nanocomposites were improved compared to those of neat polymer film [36, 37]. PVA has been broadly used as protective colloids in the manufacture of polymer emulsions, for bindings of pigments and fibers, and for the production of detergents and cleansing agents, adhesives, emulsion paints, and solution cast films [16, 17]. However, it has relatively low mechanical strength and integrity. Therefore, recently many researchers have focused on reinforcing nanocellulose within PVA matrix to improve the mechanical and thermal properties.

In this thesis polyvinyl alcohol (PVA) polymer was selected as the matrix due to its compatibility with nanocellulose suspended in water for directly mixed with the polymer. This means that the nanocellulose directly soluble in polyvinyl alcohol which don't need for chemical modification for reinforcement. For this reason poly (vinyl alcohol) was chosen to demonstrate effectiveness of nanocellulose reinforced in polymer.

2.6. Extraction of nanocellulose from bagasse

During recent years, a large number of research articles have been published on the procedures of obtaining nanocellulose from various lignocellulose materials. Several methods have been used to convert the cellulosic materials into nano-dimensional structure such as mechanical disintegration, acid hydrolysis, TEMPO-mediated oxidation and enzyme-assisted process [12]. Generally, these are broadly classified as mechanical and chemical method [12, 37].Various mechanical methods have such as steam explosion, high-pressure homogenization, high-intensity ultrasonication, and electrospinning have been used for extraction of nanocellulose. The main disadvantage this methods is high production costs and requires greater energy than chemical methods.

For this reason, a chemical pretreatment reduces energy consumption and makes the surface more hydrophobic and chemical method mostly used [12, 37-38]. Chemical method of production nanocellulose is more feasible route for production of nanocellulose from different lignocellulosic materials .The process is performed chemically to hydrolysis cellulose using acids, bases and oxidation reagents to produce nanocellulose. Acid hydrolysis is commonly used chemical methodology for extraction of nanocellulose from a great variety of sources such as various of sources, including: cotton , wood , sisal, pineapple leaves , coconut husk fibres , bananas , wheat straw , bagasse and bamboo [12]. The process is performed by strong acidic such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and hydrobromic acid (HBr); whereas phosphoric acid (H_3PO_4), maleic acid ($HO_2CCHCHCO_2H$), and hydrogen peroxide (H_2O_2) were used to a lesser extent [12,39]. However, sulfuric acid is common used for acid hydrolysis of cellulose, where it reacts with hydroxyl groups to form sulfate esters and produces stable aqueous suspension [40].

Cellulose consists of crystalline and amorphous regions. During hydrolysis treatment cellulosic fibers, the amorphous parts of cellulose are more susceptible to being attacked by acids in contrast to the crystalline part. Consequently, these microfibrils break down or hydrolysis into shorter crystalline parts with a high degree of crystalline; these are generally referred to as nanocellulose [12, 40].The acid hydrolysis process involves three stages: pretreatment process, acid hydrolysis process and post hydrolysis process.

2.6.1. Pretreatment process

Pretreatment is a series of stage in which the fiber is subjected to purification and bleaching processes to produce purified cellulose fibers. The main purpose of this pretreatment process is to remove complete or partial unnecessary non-cellulosic components such as hemicelluloses, lignin, and other impure components [40]. Various compounds such as hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2), ozone (O_3), and $NaClO_2$ are used for bleaching purpose [54]. Many researchers have been used acidified chlorite for bleaching and alkaline pretreatment for extracting nanocellulose. For example, Kumar et al. (2013), have used 0.7% (w/v) sodium chloride solution adjusted by 5% acetic acid to remove lignin and 17.5% (w/v) sodium hydroxide solution to remove hemicellulose shown in **figure 1** [42].

In similar manner, J.X. Sun et al. investigated comparative studies on isolating and characterization of cellulose from bagasse by using pretreatment with acidified $NaClO_2$ followed by alkaline treatment and found yields of 44.7 and 44.2 % [43]. The importance of pretreatment phase such as increases mechanical properties [44], avoid the influence of lignin on polymer matrix and produce purified cellulose [46-48]. For example, Suradi et al. reported that the pretreatment of the cellulose fiber could increase the strength of the fiber, thus increases mechanical properties composite materials of reinforced fiber [44].

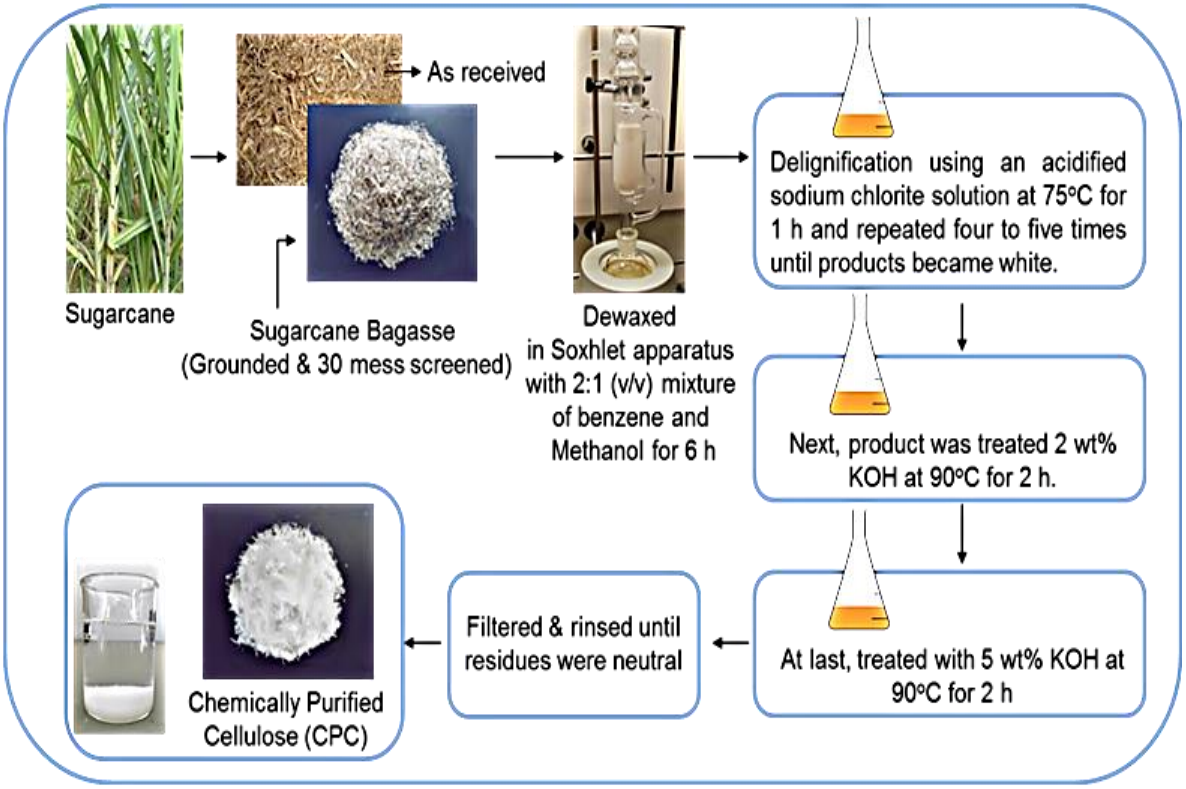

Figure 1: Pretreatment process for isolation of chemically purified cellulose from bagasse [42]

2.6.2. Acid hydrolysis process

Following the pretreatment stage, the purified and bleached cellulose is submitted to acid hydrolysis treatment stage under controlled conditions [37]. Acid hydrolysis involve high concentration of acid such as hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) as a medium. The common acid used for hydrolysis of cellulose is sulfuric acid due to its reaction with some of the hydroxyl groups (-OH) on the crystalline surface to form sulfate groups on crystalline surface (e.g., conversion of cellulose-OH to cellulose-OSO3−H+, [12, 37]. This acid hydrolysis process breakdown the amorphous regions of cellulose and isolate crystalline region that produce nanocellulose [12, 38, 40].

Different researchers have reported the extraction of nanocellulose using H_2SO_4 solution with concentration ranging 50 – 70 % (w/w) as shown in **figure 2** [27]. For instance, Kumar et al. reported the extraction of nanocellulose from sugarcane bagasse based chemically purified cellulose by acid hydrolysis (H2SO4: 64% (w/w)) at 45 °C for 60 min and obtained nanocellulose with average length (L) 250–480 nm and average diameter (D) 20–60 nm as shown in [42] . In similar manner, Teixeira et al. and Bras et al. have reported extraction of nanocellulose from bagasse by H_2SO_4 acid-hydrolysis and found nanocellulose with average length (L) ranging from 84 – 310 nm and diameter (D) with 2-12 nm [6, 7].

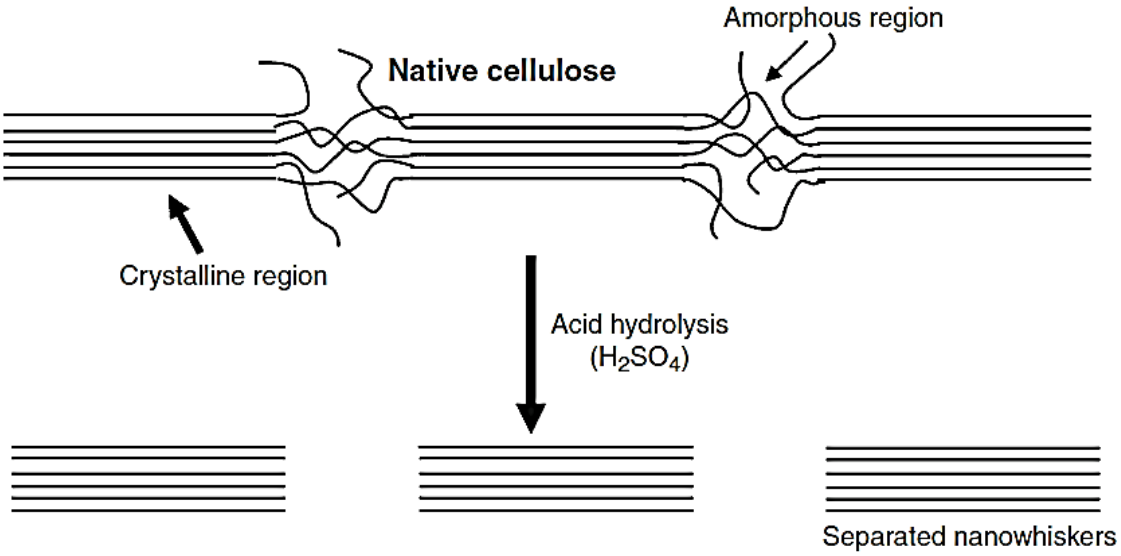

Figure 2: Schematic diagram of acid hydrolysis treatment [27]

2.6.3. Post hydrolysis stage

After the hydrolysis stage, the resulting suspension is subjected post hydrolysis treatment stage which consists of series steps: dilution of the suspension with distilled water, successive washing by centrifugations, dialysis and sonification as shown in **figure 3** [42]. The hydrolysis process is stopped by adding cold distilled water and followed successive washing by centrifugations in order remove the excess of sulphuric acid. The free acid in the dispersion is dialyzed against distilled water for several days [12, 39]. Finally, the samples subjected to sonication step in which ultrasound ensure dispersion and homogenization of nanocrystals. The suspension is freeze-dried to obtain nanocellulose product [12, 37, 40].

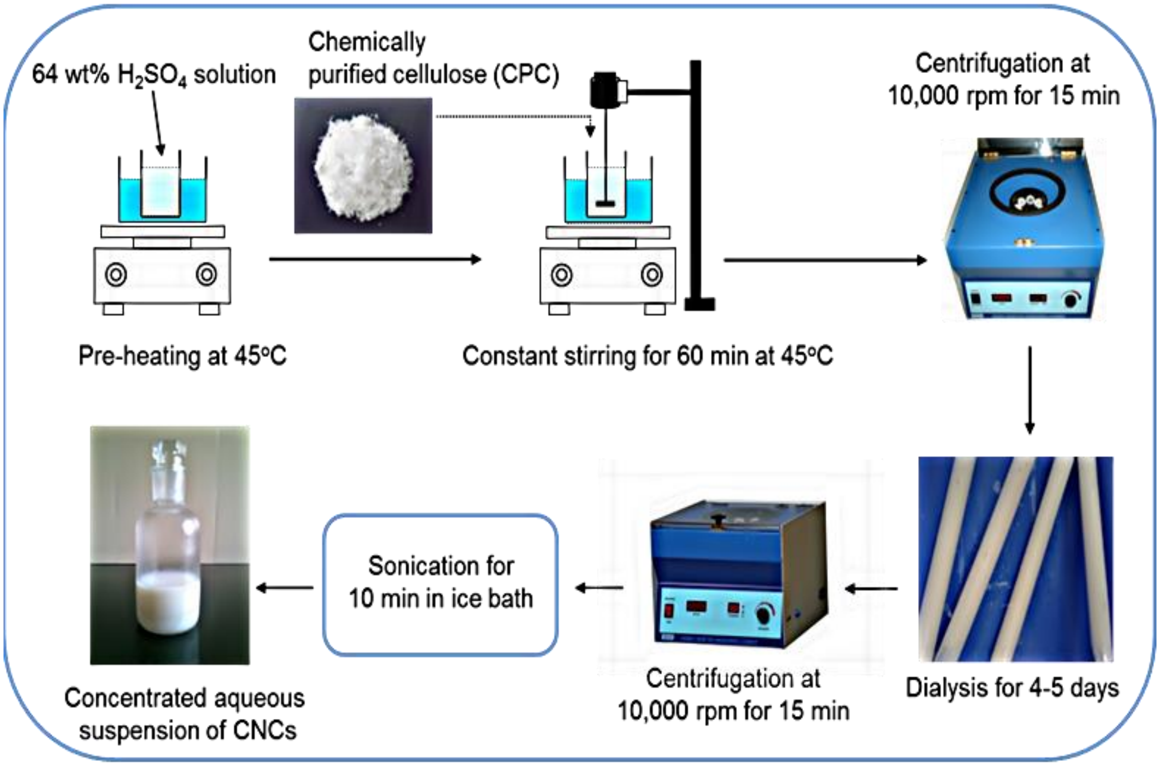

Figure 3: Hydrolysis and post hydrolysis step of nanocellulose extraction from cellulose [42]

3. Materials and Methods

3.1. Extraction of nanocellulose from sugarcane bagasse

3.1.1. Materials

Sugarcane bagasse fibers were collected from Finch Sugar Factory, Ethiopia. The samples were dried in sunlight for 5 days and ground. The grounded bagasse were sieved through 25 mesh sieve and selected further extraction of nanocellulose. The sugarcane bagasse as received and grounded and pack in polybags was shown in **figure 4**.

Chemicals and reagents**:** sodium chlorite, acetic acid, sodium hydroxide and sulfuric acid and glycerol were purchased from Niway Plc. All the chemicals are reagent grade and were used as received. Acidified 0.7 % w/v aqueous $NaClO_2$ solution, 17.5 % wt. aqueous NaOH solution and 50 % wt. aqueous H_2SO_4 solution were prepared.

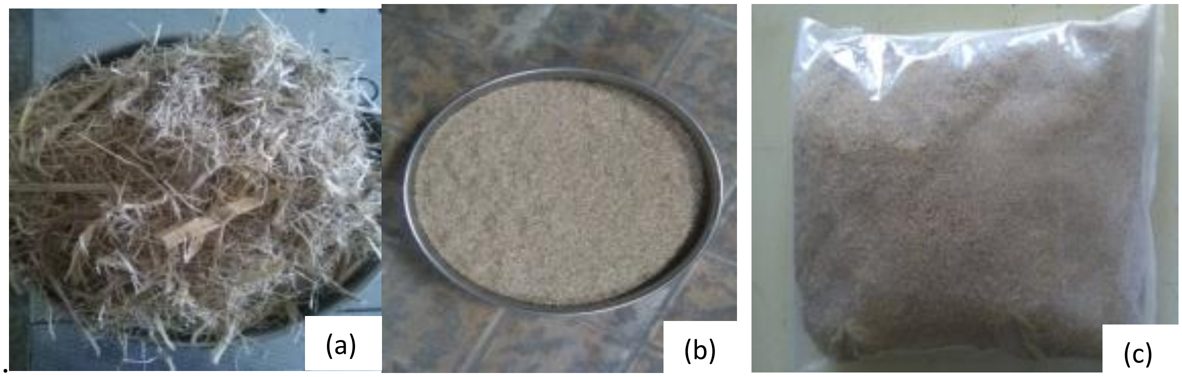

Figure 4: Sugarcane bagasse sample (a) as received from Fincha Sugar Factory (b) the grounded bagasse using laboratory mill (c) grounded bagasse was packed in polybags

3.1.2. Methods for nanocellulose extraction

To prepare nanocellulose, the cellulosic bagasse fiber was subjected three steps: **1**) bleaching step with acidified $NaClO_2$; **2**) alkaline treatment with NaOH solution; and **3**) hydrolysis step. The first two steps (bleaching and alkaline treatment steps) are preliminary steps to obtain purified cellulose fibers. After removing non-cellulosic constituents (lignin and hemicellulose), the purified cellulose was submitted to hydrolysis step for obtaining nanocellulose.

3.1.2.1. Delignification treatment step

The delignification process was conducted to remove lignin from the ground bagasse fibres using acidified sodium chlorite ($NaClO_2$) following procedure described in A. Mandal, W.Chakrabarty et al**.** Briefly, the grounded bagasse (80g) were treated with acidified 0.7 % w/v $NaClO_2$ solution at 70 °C in water bath under continues mechanical stirring. The $NaClO_2$ solution pH was adjusted to about 4 by glacial acetic acid before treating with the bagasse. The ratio of the bagasse to acidified solution was set to 1:50 (g/ml) [8].

Then, the bagasse was boiled in the $NaClO_2$ solution at 70 °C for 4 hours under continuous stirring. The bleaching process was repeated four times until the color of the bagasse fiber became white. The suspension was vacuum filtered and the solid was repeatedly washed with distilled water until yellow color disappeared or until the pH of filtrate was nearly neutral and air dried. Finally, the delignified product (holocellulose) containing hemicellulose and cellulose was obtained and further submitted to alkaline treatment for hemicellulose removal.

3.1.2.2. Isolation of cellulose

Following delignification process, the holocellulose was alkaline treated to remove lignin accordingly Kumar et al. and A. Mandal, W.Chakrabarty et al. [8, 42]. Concisely, the dried holocellulose (40g) was treated with 17.5 % wt. NaOH solution (1250 ml) at room temperature for 1 hour under continuous mechanical stirring. The suspension was vacuum filtered and washed several times with distillated water. Lastly, the purified cellulose product was air dried and submitted to hydrolysis process for nanocellulose extraction.

3.1.2.3. Extraction of nanocellulose

The nanocellulose was extracted from the purified cellulose by acid hydrolysis according to methods described in Kumar et al., and A. Mandal, and W.Chakrabarty with slight modification [8, 42]. Briefly, 10 g of purified cellulose were hydrolyzed with 50 % wt. aqueous H_2SO_4 solution (150 ml) at a ratio of 1:15 (g/ml) cellulose /H_2SO_4 solution at 45 $^{\circ}$C for 45 minutes under vigorously mechanical stirring. In order to quench the hydrolysis reaction, 10-fold of distilled water (1500 ml) were added to the reaction mixture. Then, the diluted suspension was cooled to room temperature and centrifuged at 6000 rpm for 15 minutes to remove acid solution. The sediment was rewashed with distilled water and re-centrifuged. The washing and centrifuging process was stopped when supernatant became turbid (colloidal suspension) that was when the pH of the suspension become above 5. The remaining acid was removed by dialysis (regenerated dialysis tube) for 5 days until neutral pH was achieved (pH 6 – 7). Finally, the nanocellulose suspension obtained was sonicated using probe ultrasonication (LIDI, Ethiopia) at 25 KHz for 5 minutes in water bath to obtain uniformly dispersed nanocellulose suspension. Lastly the yield was calculated by dividing the in initial weight of cellulose submitted to hydrolysis (10 g) for the weight of nanocelulose suspension dried in oven at 50 $^{\circ}$C for 24 hours. The yield was given as follows:

$$\text{Yield (\%)} = \frac{\text{initial wieght of cellulose submitted to hydrolysis}}{\text{weight of nanocellulose obatined in the suspensension}} \text{X} 100 \text{-----} (3.1)$$

3.2. Characterization of the nanocellulose

3.2.1. Particle size Analysis

3.2.1.1. Materials

The particle size analysis was performed by dynamic light scattering (DLS) using Zetasizer Nano instrument (Malvern, UK) at Leather Industry Development Institute (LIDI) (Addis Ababa, Ethiopia)**.**

3.2.1.2. Methods

The particle size analysis was performed by DLS using Zetasizer Nano instrument (Malvern, UK) at Leather Industry Development Institute (LIDI) (Addis Ababa, Ethiopia) following standard procedures .The measurement was done on nanocellulose dispersed in water with 0.1 wt. % concentration, 0.8872 cp viscosities, 344 record numbers, 0.01 material absorption, 1.59 material refractive index and 1.330 dispersion reflective indexes.

DLS measurement yields the mean particle size (Z-average) and size distribution of particles (Polydispersity index, POI) in suspension. The techniques utilize the scattering of light by diffusing particles that undergo Brownian motion and the analysis is based on the diffusion rate of the particles in the fluid. Due to non-spherical properties of nanocellulose, the particle size evaluation was determined by correlating diffusion coefficient of using Stokes – Einstein relation (hydrodynamic diameter) that the particles in dispersion undergo Brownian motion and DLS measures the translational diffusion coefficient of the particle in the dispersion. According to Stoke Einstein, larger particle slower diffusion rate and smaller particle diffuses at a greater rate.

3.2.2. Fourier transform infrared spectroscopy (FTIR) analysis

3.2.2.1. Materials

The chemical composition assessment of the raw bagasse, the treated bagasse and the nanocellulose suspension was conducted using Fourier transform infrared spectroscopy (FTIR) Analysis. FTIR spectra were obtained using Perkin Elmer FTIR spectrometer (Perkin Elmer, 65, USA) at Addis Ababa University (Addis Ababa, Ethiopia).

3.2.2.2. Methods

The chemical composition assessment of the raw bagasse, the treated bagasse and the nanocellulose suspension was conducted using FTIR analysis. The measurement was employed to examine the state of nanocellulose in comparison with the raw bagasse and to investigate the removal efficiency of other components (lignin and hemicellulose) during pretreatment steps with acidified sodium chlorite and NaOH solution. FTIR spectra were obtained using Perkin Elmer FTIR spectrometer (Perkin Elmer, 65, USA) at Addis Ababa University (Addis Ababa, Ethiopia). The analysis was done with the range of 4000 – 400 cm^{-1} in transmittance mode using KBr for bagasse and cellulose , and NaCl window for nanocellulose suspension.

3.3. Production of PVA – nanocellulose composite films

3.3.1. Materials

Polyvinyl alcohol (PVA) with a degree of hydrolysis of over 88.5 % and a molecular weight ranging between 88 and 98 kg/mol was purchased from Alkane Plc. (Addis Ababa, Ethiopia) and used as matrix for the nanocomposites preparation. The other PVA specifications: viscosity 51.8. mPa.s, volatility 2.7 %, content sodium acetate 0.6 %, ash content 0.4 % and purity 96.7 %. For avoiding sticking of the film to Petri dish during dying, glycerol was used on the surface of Petri dish and purchased from micro Plc. (Addis Ababa, Ethiopia). From the produced nanocellulose suspension, four sets of nanocellulose suspension (0 % wt., 3 % wt., 5 % wt. and 7 % wt.) with respect to weight of PVA was used as reinforcement in PVA matrix. For comparative study, other two sets from ground bagasse suspension (5 %wt. B) and from purified cellulose suspension (5 %wt. C) were prepared. Petri dishes and other laboratory equipment for solvent casting were taken from the lab. (School of Chemical and Bio Engineering, Addis Ababa).

3.3.2. Methods

The nanocellulose–PVA composite films were prepared by solvent casting method. Accordingly, the aqueous solution of PVA was prepared by dissolving 5g of PVA powder in 50 ml of distilled water at 80°C for 2 hours under manual stirring until the PVA fully dissolved and clear jelly like solution was formed. The solution was cooled to room temperature while stirring and different amount of nanocellulose suspensions were added to PVA solution under continuous stirring until the solution became viscous.

In order to study effect of varying nanocellulose amount on the composite, four sets of nanocellulose suspension (0 % wt., 3 % wt., 5 % wt. and 7 % wt.) with respect to weight of PVA were added to the PVA solutions to produce neat PVA (PVA/ 0%NC), PVA- reinforced with 3 % wt. nanocellulose suspension (PVA/ 3 %NC) , PVA- reinforced with 5 % wt. nanocellulose suspension (PVA/ 5 %NC) and PVA- reinforced with 7% wt. nanocellulose suspension (PVA/ 7 %NC). For comparative study and analysis of the reinforced nanocellulose composite, other two sets from ground bagasse and purified cellulose suspension were prepared and reinforced within the PVA matrix. Thus, the bagasse –reinforced PVA composite (PVA/ 5 %B) and purified cellulose –reinforced PVA composite (PVA/ 5 %C) were also prepared by adding bagasse suspension (5 % wt.) and purified cellulose suspension (5 %wt.) to the PVA solution respectively. Formulation for the production of PVA-nanocellulose composites films were shown in **table 1.**

Table 1: Formulation for the production of PVA-Nanocellulose composites films

Composite	Amount of PVA used (wt. %)	Amount of reinforcement used (wt. %)	Glycerol (wt. %)
PVA/ 0%NC	100	0 wt % nanocellulose	1.5
PVA/ 3%NC	97	3 wt % nanocellulose	1.5
PVA/ 5%NC	95	5 wt % nanocellulose	1.5
PVA/ 7%NC	93	7 wt % nanocellulose	1.5
PVA/ 5%B	95	5 wt % bagasse	1.5
PVA/ 5%C	95	5 wt % cellulose	1.5

3.4. Characterization of PVA/ nanocellulose composite films

Characterization of the PVA/ nanocellulose composite films were performed by using various analytical techniques such as water absorption capacity, scanning electron microscopy (SEM) and mechanical properties.

3.4.1. Water Absorption Test

One of the factor that affects the properties is PVA/ nanocellulose composite films is water absorption capacity of the film. Reinforcement PVA with nanocellulose exhibit change in water absorption capacity. The test was conducted to evaluate effectiveness of reinforcement of the films in terms of water absorption capacity of the reinforced polymer.

3.4.1.1. Materials

The prepared PVA/nanocellulose composite films were taken and pieces were cut from each samples using scissors. Oven drier was used for drying the films. Desiccator and micro balance were used for cooling the film and weighting the films respectively.

3.4.1.2. Methods

The water absorption behavior of the composite films were evaluated by immersing in distilled water. For the absorption test, the PVA/nanocellulose composite film was dried in oven at 50 $^{\circ}$C for 24 hours. Then, the films were cooled in desiccator and the weight of each film was taken immediately. The known weights (W_o) of the initial films were fully immersed in distilled water at room temperature for one minute. The films were taken out off the immersion and the excess water on the surface of the films were removed by using filter paper, then the final weight (W_t) was measured and recorded. The percentage of water absorption was calculated for each sample from the increase in initial weight using following formulas:

$$\text{Water Absorption } (\%) = \frac{W_t - W_o}{W_o} \times 100 \text{ --------------------------- } (3.2)$$

Where W_t and W_o are weight of wet samples and weight of the initial samples respectively.

3.4.2. Scanning electron microscopy (SEM)

To evaluate effectiveness of reinforced polymer in relation to surface morphology, scanning electron microscopy was employed. The SEM micrographs provides helpful information about distribution pattern of the reinforced nanocellulose phase in the PVA matrix such as morphology of the dispersed polymer matrix, homogenous dispersion and tendency of agglomeration. It also reveals that the bonding network between PVA matrix and the nanocellulose whether rigid percolation reinforced network was formed or not.

3.4.2.1. Materials

Polyvinyl alcohol reinforced with 5 % nanocellulose (PVA/ 5%NC) film was taken as a sample for morphology analysis. Cutter was used to get small portion of PVA/ 5% NC sample for analysis. Gold was used for sputtering of the film using sputtering apparatus. to prevent charge build-up during SEM analysis. JEOL JSM - IT300 scanning electron microscope was used for analyzing the surface morphology of the film at Leather Industry and Development Institute (LIDI) (Addis Ababa, Ethiopia).

3.4.2.2. Methods

In order to determine the morphology and uniform dispersion of nanocellulose in the PVA matrix, the SEM measurement was conducted on PVA/nanocellulose composite film of 5 wt. % NC loading. The morphology of the PVA/ 5 %NC composite film was analyzed with standard procedure of morphology measurement at LIDI (Addis Ababa Ethiopia). A small sample of the PVA/ 5 %NC composite film was cut and taken for coating. Then, the sample was sputtered with gold and the morphology of the film was investigated by using a JEOL JSM-IT300 scanning electron microscope. The image was obtained under accelerating voltage of 20 KV at (LIDI) (Addis Ababa, Ethiopia).

3.4.3. Mechanical Properties

The effectiveness of reinforcing nanocellulose in PVA matrix was also evaluated in terms of improvement in mechanical properties. High surface area, aspect ratio, high tensile strength and young`s modules of nanocellulose are dedicated to improve mechanical properties of the matrix and effectiveness of reinforcing ability. The mechanical properties of nanocomposites were studied from interaction between nanocellulose and PVA matrix. These improvement in mechanical properties such as tensile strength and elongation at break can be obtained from mechanical test in relation to reinforcement.

3.4.3.1. Materials

PVA / nanocellulose composite films were used as material for the mechanical tests. Tensile strength testing, thickness gauge, cutting machine and steel die of standard dimension equipment were used.

3.4.3.2. Methods

The tensile strength and elongation at break of the composite films were measured on tensile testing machine as follows: the composite film with dimension of 10mm (width) X 0.1 mm (thickness) X 40 mm (length) were cut and mounted in the grips of tensile testing machine. The thickness and width of the film were measured with thickness gauge and steel ruler respectively. The test was carried out at room temperature until the film was broken by applied force. As the film breaks, the distance between the two grips was measured and the maximum forces were taken. The tensile strength and percentage elongation at break were obtained by formula (3.3) and (3.4) respectively.

$$\text{Tensile strength of the film} = \frac{\text{Maximum breaking load applied}}{\text{cross sectional area of the film}} ---------(3.3)$$

$$\text{Percentage elongation of the film} = \frac{\text{Final length at break - initial length}}{\text{initial length}} ----(3.4)$$

The initial length is distance between the jaws before applying load and the final length is between the jaws in mm when the film was broken due to maximum load application.

3.5. Evaluation of effectiveness of reinforcement

In order to evaluate the effectiveness of the reinforcement, comparative analysis between the nanocellulose reinforced PVA and neat PVA was done in terms of water absorption values and mechanical properties. Similarly, nanocellulose reinforced PVA was compared with bagasse and cellulose reinforced PVA to evaluate effectiveness of incorporating nanocellulose within PVA polymer matrix. In order to understand the effectiveness easily, the reinforcement brought on the PVA matrix and with PVA in relation to mechanic improvement and water absorption capacity were clustered into regions.

3.5.1. Materials

Data from tensile strength values, elongation at break values, water absorption values and morphology values were used to evaluate the effectiveness of the reinforcement.

3.5.2. Methods

Effectiveness evaluation of reinforcement was made by comparative and cluster analysis methods. The results obtained from water absorption values, tensile strength and percentage elongation at break values and SEM morphology of the reinforcement were taken and analyzed. Comparative and cluster analysis were made between samples and with control samples. The comparisons were done between the nanocellulose reinforced PVA films with neat PVA film , with bagasse and cellulose reinforced PVA composite films. Results were compared between films well as with neat film.

Variations observed between reinforced PVA films and neat PVA were used to evaluation the effectiveness of the incorporating nanocellulose in the PVA polymer matrix. The comparative results were analyzed using comparative analysis and cluster analysis for easily understanding of the effectiveness reinforcement brought on the PVA matrix in relation to mechanical properties and water barrier properties.

4. Results and Discussion

4.1. Extraction of nanocellulose from sugarcane bagasse

Nanocellulose suspension obtained from sugarcane bagasse after delignification alkaline bleaching and acid hydrolysis was given in **figure 5**. The suspension was lighter than the delignification and bleaching steps. This was due to the removal of the lignin and hemicellulose constitutes. The amount of nanocellulose in the suspension was determined by dying in the oven for 24 hours at 105 °C and the suspension concentration of nanocellulose was found 0.0125 g/ml. After knowing the concentration of nanocellulose in the suspension, the suspension yield was calculated using equation (3.1).

The yield of nanocellulose with respect to the initial amount of dried cellulose used was found 40 %. With long reaction time, higher concentration of the acid and acid to fiber ratio increment, the decrement in yield was expected. The acid hydrolysis was able to hydrolyze the cellulose chains to separate the crystalline part from the amorphous part. This process breaks down the disordered and the amorphous parts of cellulose and produced nanocellulose which was a nanoscale dimension used for reinforcing in PVA matrix.

Figure 5: The nanocellulose suspension obtained from sugarcane bagasse after pretreatment and hydrolysis process

4.2. Characterization of the Nanocellulose

4.2.1. Particle size analysis

The results of particle size analysis of the nanocellulose suspension by DLS were given in **figure 6** and summarized in **table 2**, where particle size distribution shown as function of particle diameter. The distribution showed trimodal distribution (**figure 6**) shown by peak I, peak II and peak III with corresponding particle size of 80.19 ±17.01 nm, 442.8 ±173.4 nm and 5285 ± 416.5 nm respectively. The mean particle size obtained was 348.6 nm showing that the obtained result was nanosize derived from acid hydrolysis of sugarcane bagasse and it confirms that the product was nanocellulose.

Table 2: Particle size analysis of nanocellulose suspension resulted by DLS.

DLS Result			
Z-Average (d.nm) : 348.6		**Size (d.nm)**	**% Intensity**
PDI : 0.600	**Peak I**	80.19	14.6
Result quality : Good	**Peak II**	442.8	79.8
	Peak III	5282	5.6

The percentage shown for each peak was represented the contribution of each peaks toward the overall number of particles counted. In the first peak (**peak I**), the recorded particle size was 80.19 nm and it accounts only 14.6 percent of the overall intensity distribution. This was interpreted as the diameter of the nanocellulose in the suspension. Using imaging technique of measurement (field microscope and transmission electron microscope), different authors have described nanocellulose has a rod-like shaped with diameter ranging from 3 nm to 100 nm. In the second peak (**peak II**), the particle size obtained was 442.8 nm and it account 79.8 percent of the overall intensity distribution. This peak was interpreted as the length of nanocellulose in the suspension. From this peak, it was clear that most of the particle in suspension were found within this range. In the third peak (peak III), the particle size was 5285 nm that accounts only about 5.6 percent of the overall intensity distribution. This result was represented nanocellulose suspension contains small amount of agglomerated nanocellulose arisen from either concentration of the nanocellulose within suspension or from attraction of nanocellulose through hydrogen bonding.

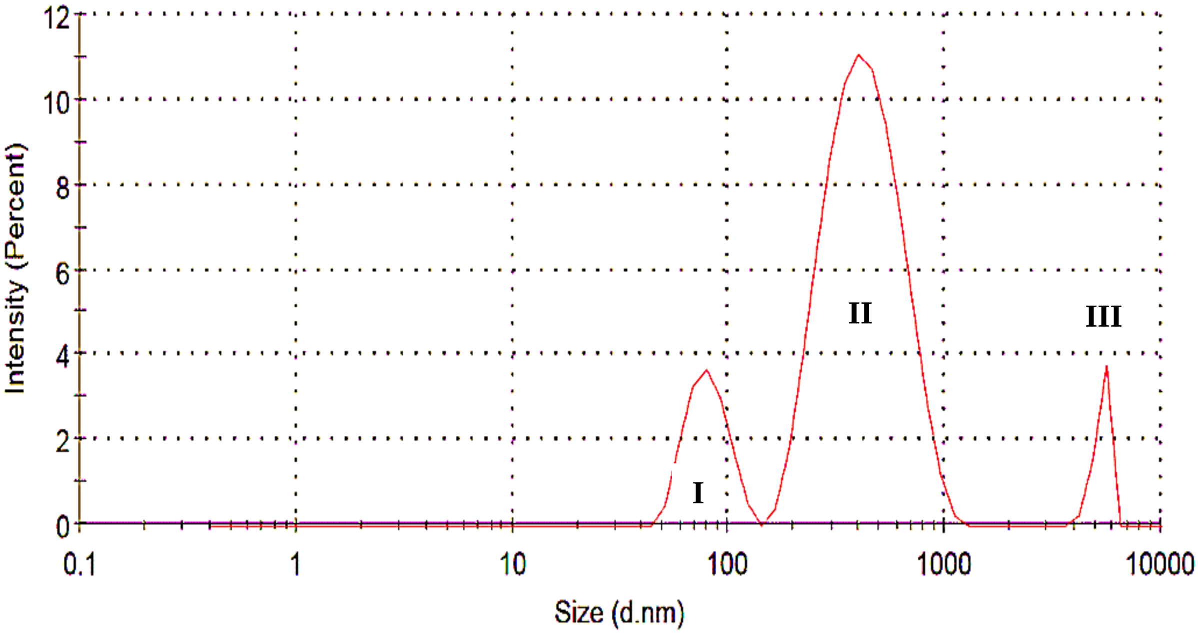

Figure 6: Particle size distribution of nanocellulose suspension obtained from DLS measurement.

The polydispersibility index (PDI) for the analysis was found 0.6 which was in the normal range. This result indicates the obtained analysis had good in uniformity and narrower size distribution compared higher PDI (PDI > 0.7). Higher PDI (PDI > 0.7) with non-uniform and very broad size distribution.

Thus, from DLS studies showed the obtained result was nanosize dimension. Hence, nanocellulose in the form of a stable dispersion was extracted from sugarcane bagasse. The minimum nanocellulose size obtained was 80.19 nm and larger size was 442.8 nm. The rest nanocellulose was in the range of 100 to 1000 nm that account about 79.8 % percent of the total intensity. The nanocellulose suspension was used for reinforcement in polymeric matrix for improving properties of the host matrix.

4.2.2. FTIR results

The FTIR result of sugarcane bagasse, cellulose and nanocellulose are given in **figure 7** and summarized in **table 3.** Accordingly, all the samples were showed two main transmittance region in range of 4000 – 2000 cm^{-1} (**figure 7a**) and 2000 – 400 cm^{-1} (**figure 7b**) . The spectra of sugarcane bagasse fibers, cellulose and nanocellulose were given as percentage of transmittance versus wave number.

All the three spectra showed broader and intense peak at 3400 cm^{-1} for the bagasse, cellulose and nanocellulose in **figure 7a**, which could be characterized the stretching bond of polysaccharide O-H group. The peak located at 2900 cm^{-1} for the bagasse and cellulose spectra were due to C-H symmetrical stretching that interpreted as presence of small amount of polysaccharide waxes and oil in the raw material and the cellulose. This implies that extraction of waxes and oil was required during pretreatment such as soxhlet extraction. The absence of this peak in nanocellulose spectrum implies that physico-chemical treatment applied during hydrolysis and post hydrolysis treatment was possibly able to remove this peak from the spectrum.

The observed peak at 1632 cm^{-1} in the bagasse fiber was assigned to the water absorbed to the bagasse fibers (**figure 7b**). This peak was decreased in cellulose spectrum due to removal of hemicellulose during treatment step. In the bagasse fiber spectrum, the peak located at 1512 cm^{-1} indicates the C=C stretching aromatic ring of lignin component. The peak at 1248 cm^{-1} in the bagasse fiber spectrum was associated to C - O stretching aryl groups of lignin. In similar manner, the peak observed at 1446 cm^{-1} (from methoxy O - C) and at 1608 cm^{-1} (from C = C stretching of aromatic ring) implies the presence of lignin in the raw sugarcane bagasse. However, all the spectra were disappeared in both cellulose and nanocellulose confirming that the removal of lignin during treatment steps with acidified sodium chlorite and NaOH solution. This shows the effectiveness of the applied chemical treatment for the removal of lignin component from the bagasse fibers. The other peak located at 832 cm^{-1} in bagasse spectrum represents lignin and it’s absent in cellulose and nanocellulose spectra indicates the effectiveness of applied pretreatment for removing nanocellulose.

The peaks observed within the range of 1384 – 1328 cm^{-1} shows the bending vibration of C-H and C-O group in polysaccharide aromatic rings of cellulose and hemicellulose. These peaks were intense in bagasse fibers spectra and its intensity was reduced both in cellulose and nanocellulose. This reduction implies the hemicellulose removal of during treatment steps (bleaching with NaOH solution). Finally, the detected peak at 1160 cm^{-1} and 896 cm^{-1} correspond to the cellulose with C-O-C stretching of pyranose ring and C-H stretching of β-glycoside bond of cellulose respectively. Similarly, the peak shown on the three spectra at about 1432 cm^{-1} represents the cellulose component.

Table 3: FTIR characteristic peaks of sugarcane bagasse fibers, cellulose and nanocellulose

Wave number (cm^{-1})	FTIR Spectra of the bagasse, Cellulose and nanocellulose (cm^{-1})			Assignment of the peak
	Bagasse	Cellulose	Nanocellulose	
3400	3400	3400	3400	O- H stretching of cellulose
2900	2900	2900	-	Polysaccharide waxes and oils
1632	1632	1632	-	Water aborted to bagasse fiber
1608	1608	-	-	C=C stretching of lignin
1512	1512	-	-	Aromatic ring of C=C lignin
1446	1446	-	-	methoxy - O- C of lignin
1432	1432	1432	1432	C-H stretching of cellulose
1384 - 1318	1384 - 1318 (intense)	1384 -1318 (smaller)	1384 -1318 (not intensity)	C-H and C-O groups in cellulose and hemicellulose
1248	1248	-	-	C-O stretching of aryl group of lignin
1160	1160	1160	1160	C-O-C stretching of cellulose
896	896	896	896	C-H stretching of cellulose
832	832	-	-	Aromatic ring of lignin

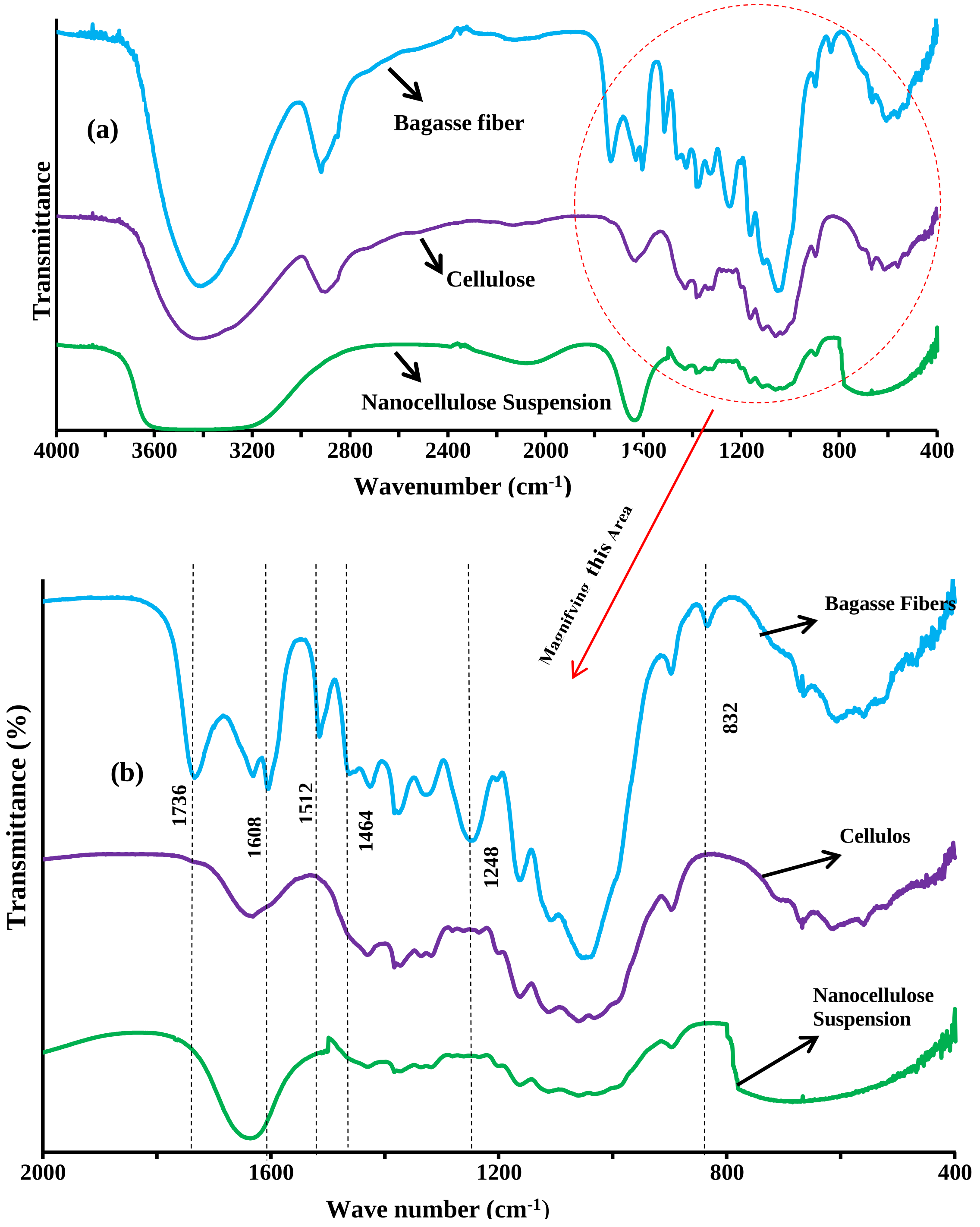

Figure 7: The FTIR Spectra of Bagasse Fiber, Cellulose and Nanocellulose Suspension (a) FTIR spectra from 4000 cm^{-1} to 400 cm-1 and (b) FTIR spectra from 2000 cm^{-1} to 400 cm^{-}

4.3. PVA – nanocellulose composite films

The PVA- nanocellulose films produced by solvent casting were given in **figure 8.** Flexible and transparent films with approximately 0.1 mm thickness were obtained. The films were designed as PVA/0%NC, PVA/3%NC, PVA/5%NC and PVA/ 7%NC for the nanocellulose reinforced in PVA ; PVA/5%B for bagasse - reinforced in PVA and PVA/ 5%C for cellulose - reinforced in PVA and further characterized by a variety techniques.

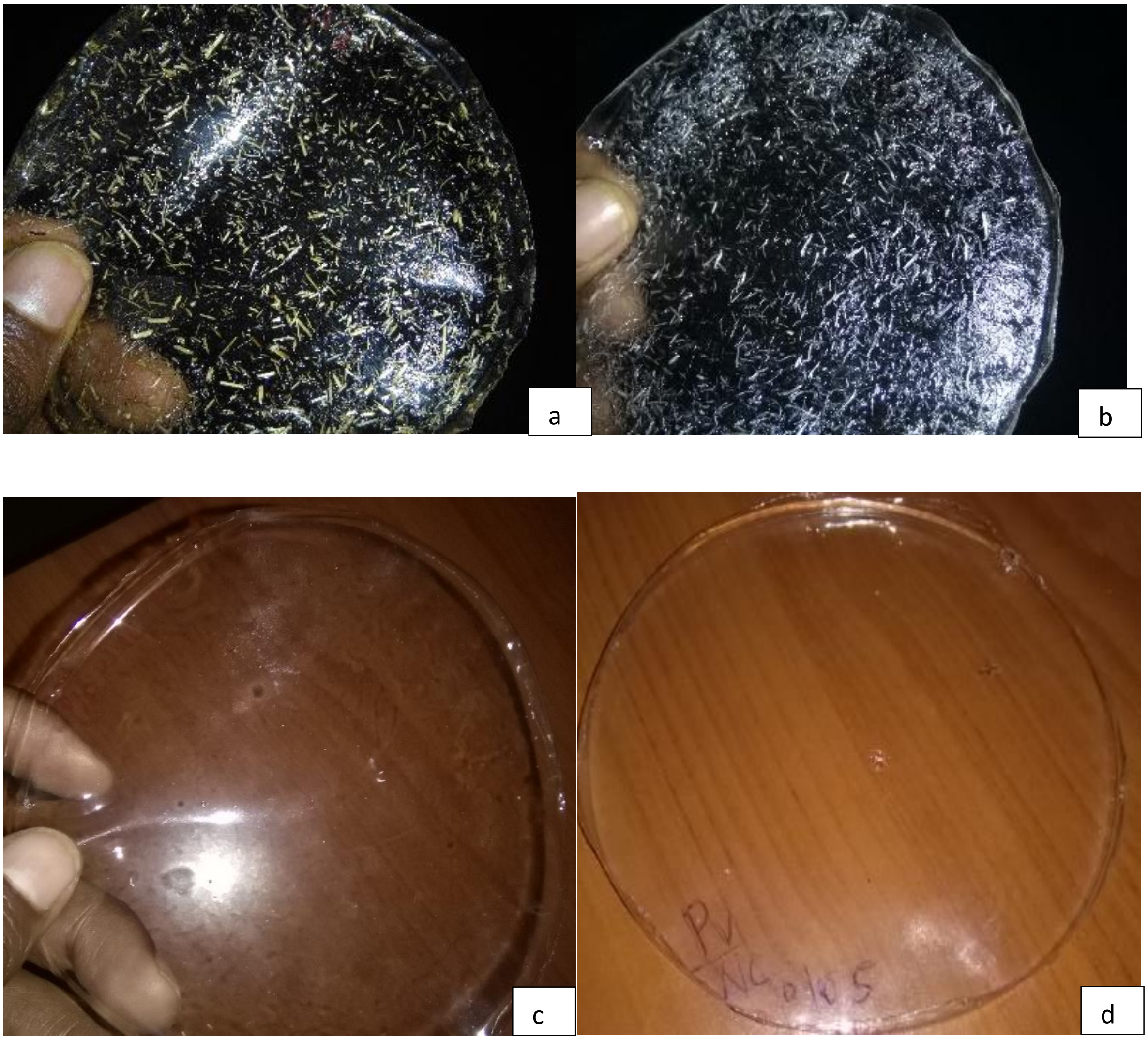

Figure 8: The composite films (a) PVA/5 % B, (b) PVA/5 % C, (c) PVA/0 % NC and (d) PVA/5% NC

4.4. Characterization of the PVA/ Nanocellulose Composite Films

4.4.1. Water Absorption

The measured percentage water absorption values of the films were given in **table 4** and **5**. The values shown were represented the water absorption capacity of the nanocellulose reinforced in PVA polymer matrix for different loading rate of nanocellulose and the water absorption capacity of the bagasse, cellulose and nanocellulose reinforced in PVA polymer matrix. In all cases, the absorption capacity were reduced with increase the amount of nanocelulose **(table 4)** and with the type of reinforcement (bagasse and cellulose) compared to the neat PVA polymer **(table 5).** According to the result, the reinforcement could able to reduce the water absorption of the PVA from 82% for neat PVA to 59 % for PVA/7 % NC composite (**table 4**) and from 82 % for PVA to 76 % for PVA/ 5% B, 71 % for PVA/ 5% C and 64 % for PVA/ 7% NC (**table 5**).

Table 4: The measured water absorption capacity (%) of the PVA films as function of nanocellulose amount.

Samples	**Water Absorption Capacity (%)**
PVA/0 %	82
PVA/ 3% NC	68
PVA/ 5% NC	64
PVA/ 7% NC	59

Table 5: The measured water absorption capacity (%) of the PVA films as function of reinforcement type (bagasse, cellulose and nanocellulose).

Samples	**Water Absorption Capacity (%)**
PVA /0%	82
PVA/ 5%B	76
PVA/ 5% C	71
PVA/ 5% NC	64

Figure 9 and **10,** shows percentage water absorption capacity of films produced by reinforcing PVA polymer matrix with nanocellulose and fibers, and neat PVA. According to the result, the neat PVA film resulted in higher water absorption capacity than the corresponding samples that were reinforced with nanocellulose, bagasse fiber and cellulose. This reduction in water absorption capacity shows that polymer matrix that contain nanocellulose and fibers (cellulose and bagasse) have a good preventive ability against water. This could be related two possible reasons.

The first possible reason could be due to morphology of nanocellulose (voids, free volume, crystal size and degree of crystallinity) that could reduce the diffusion of water molecules in the material. The presence of the nanocellulose reduce the water sorption by alter diffusion pathway of water molecules from direct diffusion to a tortuous path that leads to the improvement in water barrier by producing a tortuous pathway [**figure 9**].

The second possible reason for reduction in water absorption capacity of the films could be arise from bagasse fiber composition such as hemicellulose and lignin that plays important roles in water absorption and storage. This indicate that fiber with higher content of hemicellulose absorb more water than fiber that partially or completely freed of hemicellulose by pretreatment. Reduction in water absorption capacity for cellulose reinforced with PVA matrix relative to bagasse reinforced PVA arise from the pretreatment used to remove hemicellulose, lignin, relative uniform distribution and the size aspects. This aspects such pretreatment, size and uniform distribution made the composite ability to reduce water absorption. The results were similar with other studies such as Lani et al. [50]. Much reduction in water absorption capacity was observed when the PVA reinforced with nanocelulose. The percentage water absorption capacity of PVA/nanocellulose composite was lower and this values depend on the amount of nanocellulose loading. It can be noticed that the presence of nanocellulose in PVA matrix was able to reduce water uptake of the composite, indicating that the nanocellulose was able to increase tortuosity in composite and make the water absorption of the composite to be lowered

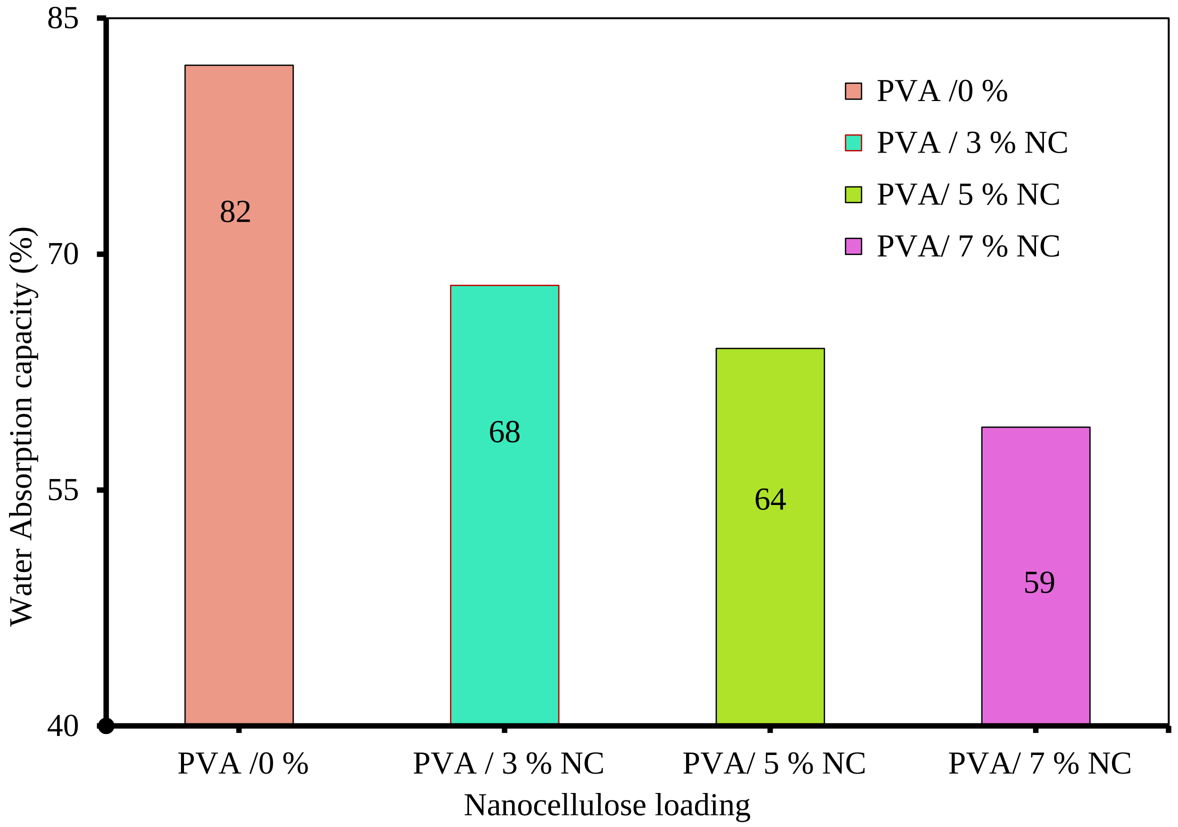

Figure 9: Water absorption of PVA/NC composite with various amount of nanocellulose loading

The percentage water absorption for PVA/ nanocellulose, PVA/bagasse fiber and PVA/ cellulose were shown in **figure 10**. The results clearly shows that effectiveness brought by incorporating the nanocellulose, cellulose and bagasse fibres into the PVA polymer matrix. For the same amount of loading, the water absorption capacity of the composite films were changed compared to neat PVA film. Compared to the neat PVA polymer, all the reinforcement showed reduction in water absorption. For 5 % of loading, the water absorption were found 82 % for neat PVA polymer , 76 % for PVA reinforced with bagasse fibers, 71% for PVA reinforced with cellulose and 64 % for PVA reinforced with nanocellulose . This change could be arise from size (nanoscale, micro scale), chemical composition (hemicellulose, lignin), interaction between the polymer matrix and the reinforced materials.

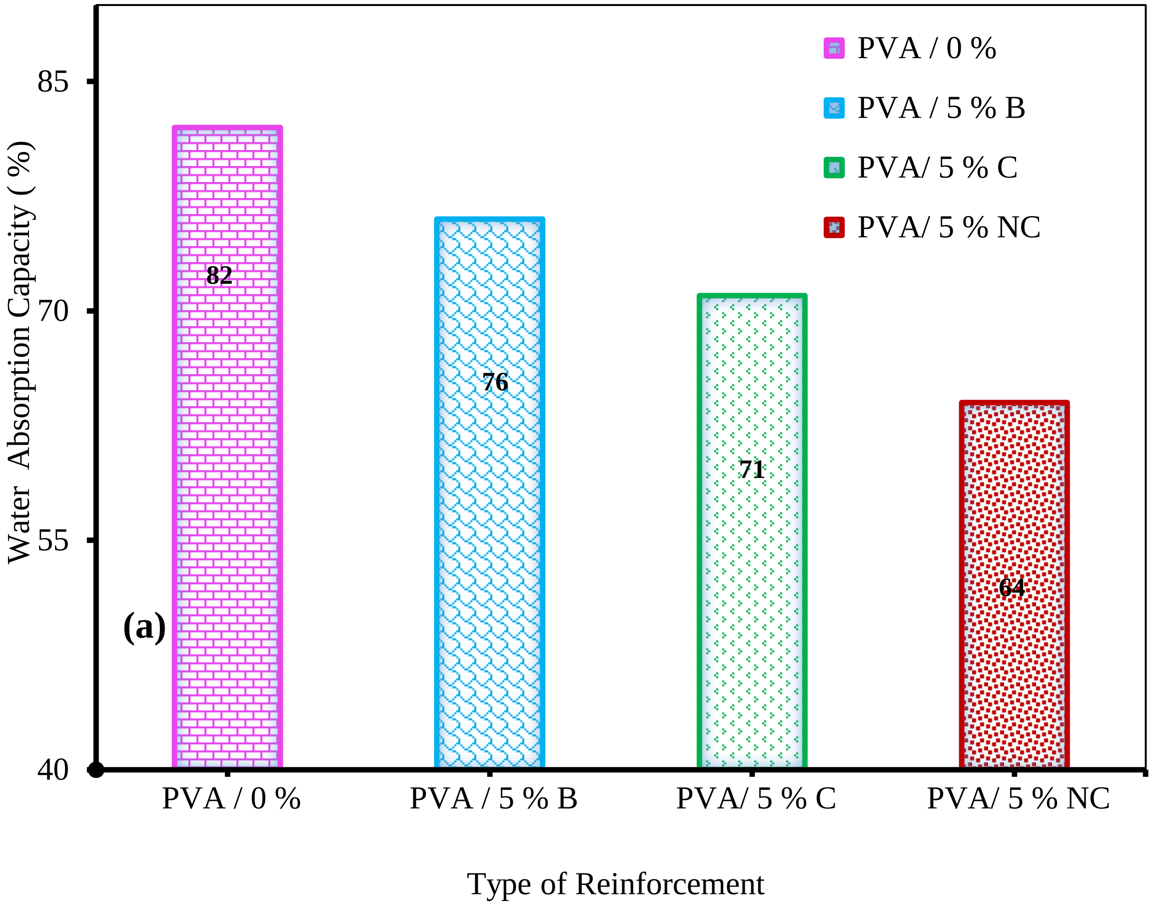

Figure 10: Water absorption capacity of PVA reinforced with the same amount, 5%wt., of sugarcane bagasse, cellulose and nanocellulose.

4.4.2. Morphology analysis by SEM

The SEM micrograph for the PVA/ 5 %NC composite film morphology of the nanocellulose/PVA were given in **figure 11** and **12**. **Figure 11** indicates the morphology PVA/ 5 %NC composite film produced by forming network like structure between PVA matrix and the nanocellulose. **Figure 12** indicates the morphology PVA/ 5 %NC composite film produced by homogenous dispersion of nanocellulose within the PVA matrix.

The SEM micrograph for the PVA/ 5 %NC composite film showed web like network structure that was formed as a result of reinforcement (**figure 11**). This network represents the interaction between PVA polymer and nanocellulose by forming rigid percolation reinforced network within host matrix and strong interaction between the two constituents through hydrogen bonding.

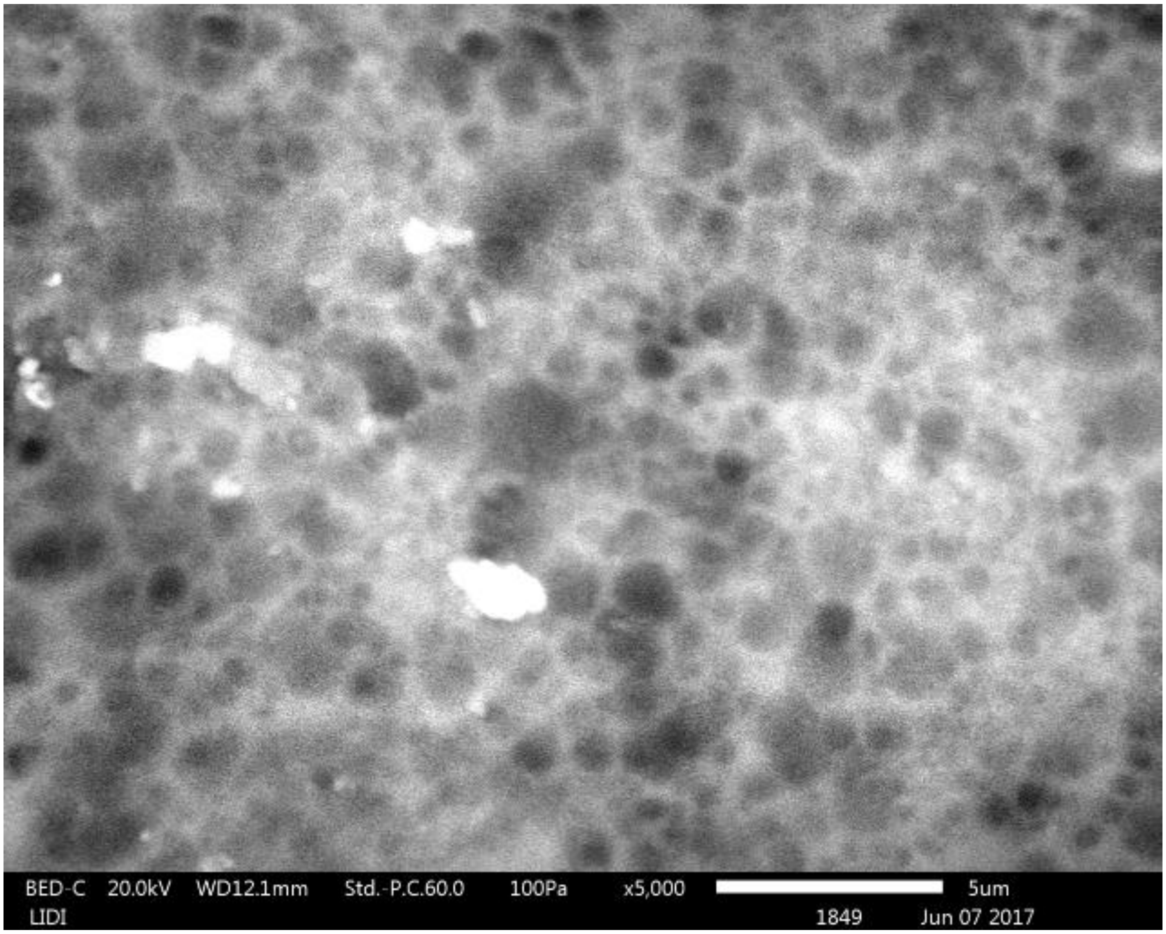

Figure 11: SEM image of PVA/ 5 %wt. nanocellulose composite film showing the web like bonding between nanocellulose and PVA matrix

The uniform distribution of nanocellulose within the host matrix also shown by SEM analysis. For the PVA/ 5% NC composite film analyzed by SEM, the distribution pattern of the nanocellulose in the continuous phase PVA matrix showed uniform distribution (**figure 12**). As it can be seen from the figure, the nanocellulose was uniformly distributed in the PVA matrix, but there were some white dotted structure observed over surface of the composite.

This white dots could possibly arise from bubbles generated during PVA nanocomposites film production. During mixing process of PVA with nanocellulose suspension and casting on petri dish, bubbles were generated. During homogenization with ultrasonication, some bubbles were left in the solution and appeared on the film during casting process which affect the morphology and mechanical properties of the composite. Also this white dots could be generated during SEM analysis that can possibly form surface charging of the film.

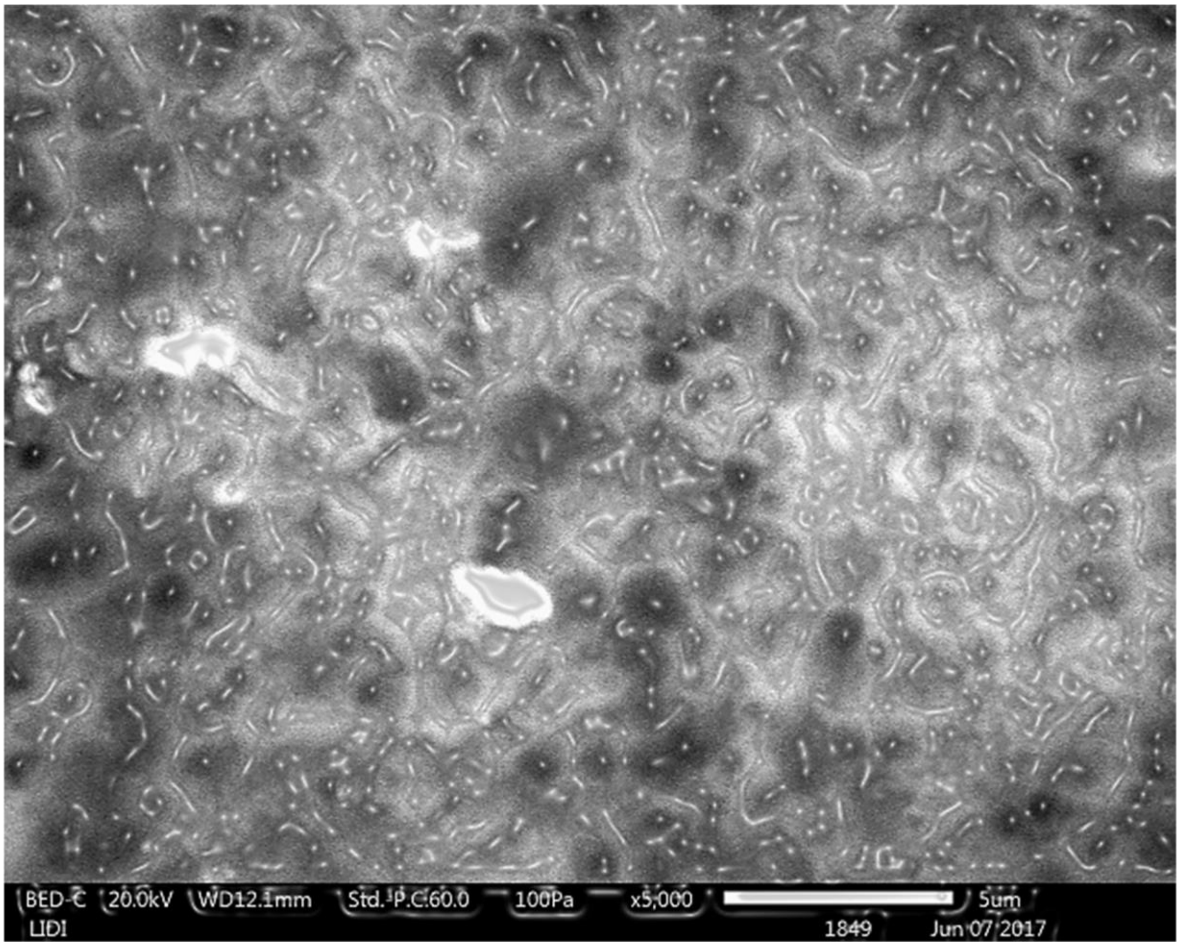

Figure 12: SEM image of PVA/5%wt. nanocellulose composite film showing the homogenous distribution of nanocellulose within the PVA matrix.

4.4.3. Mechanical properties

The measured mechanical properties of the reinforced PVA nanocomposites films were given in **table 6** and **figure 13** and **14.**

Table 6: The tensile strength and elongation at break of the PVA reinforced with nanocellulose, cellulose and bagasse fibres films.

Composite	Tensile strength (MPa)	Elongation at break (%)
PVA/ 0%NC	33	358
PVA/ 3%NC	40	161
PVA/ 5%NC	53	147
PVA/ 7%NC	39	302
PVA/ 5%B	34.8	329
PVA/ 5%C	37.7	306

As nanocellulose content increased from 0 % NC (neat PVA) to 3 % NC, 5 % NC and 7 % NC, the tensile strength of the composite films were increased from 33 MPa to 40 MPa for the 3 % NC loading, 53 MPa for 5 % NC loading and then decreased to 39 MPa for 7 % NC loading (**figure 13)**. However, the elongation at break was decreased from 358 (neat PVA) to 161 for PVA/ 3% NC, again to 147 for PVA/ 5% NC and to 302 for PVA/ 7% NC (**figure 13**). The tensile strength was increased with increasing nanocellulose loading up to 5 % NC and followed by decrement at 7 % NC nanocellulose loading. In opposite to tensile strength, the elongation at break was decrease with increasing nanocellulose loading up to 5% NC and followed by increment at 7 % NC nanocellulose loading. According to Cho et al**.,** high tensile strength & tensile modules were obtained in the range of 4 up to 5 % NC nanocellulose loading rate. The increment in tensile strength and decrement in elongation at break related to strong interaction between PVA matrix and nanocellulose that could be able to produce stiff and continuous network of nanocellulose linked through H-bonding by improving the nanocomposite properties [51-53].

The increment in tensile strength and decrement in elongation at break up to 5 % NC nanocellulose loading were resulted from percolation phenomena that improves the mechanical properties of the reinforced composite films. In addition to this, uniform dispersion of nanocellulose within PVA matrix could able to produce a continuous rigid network as well as strong interaction between nanocellulose and PVA matrix. This formation was resulted in composite films with improved mechanical properties.

The reduction in tensile strength and increment in elongation at break at 7 % NC loading, was related to percolation effect [52**]**.The interaction between nanocellulose and PVA matrix could partially hinder the formation of expected percolating nanocellulose network. Also inadequate dispersion and poor adhesion between nanocellulose and PVA matrix, can resulted in reduction of tensile strength and tensile modules at 7 % NC loading and increment in elongation at break .

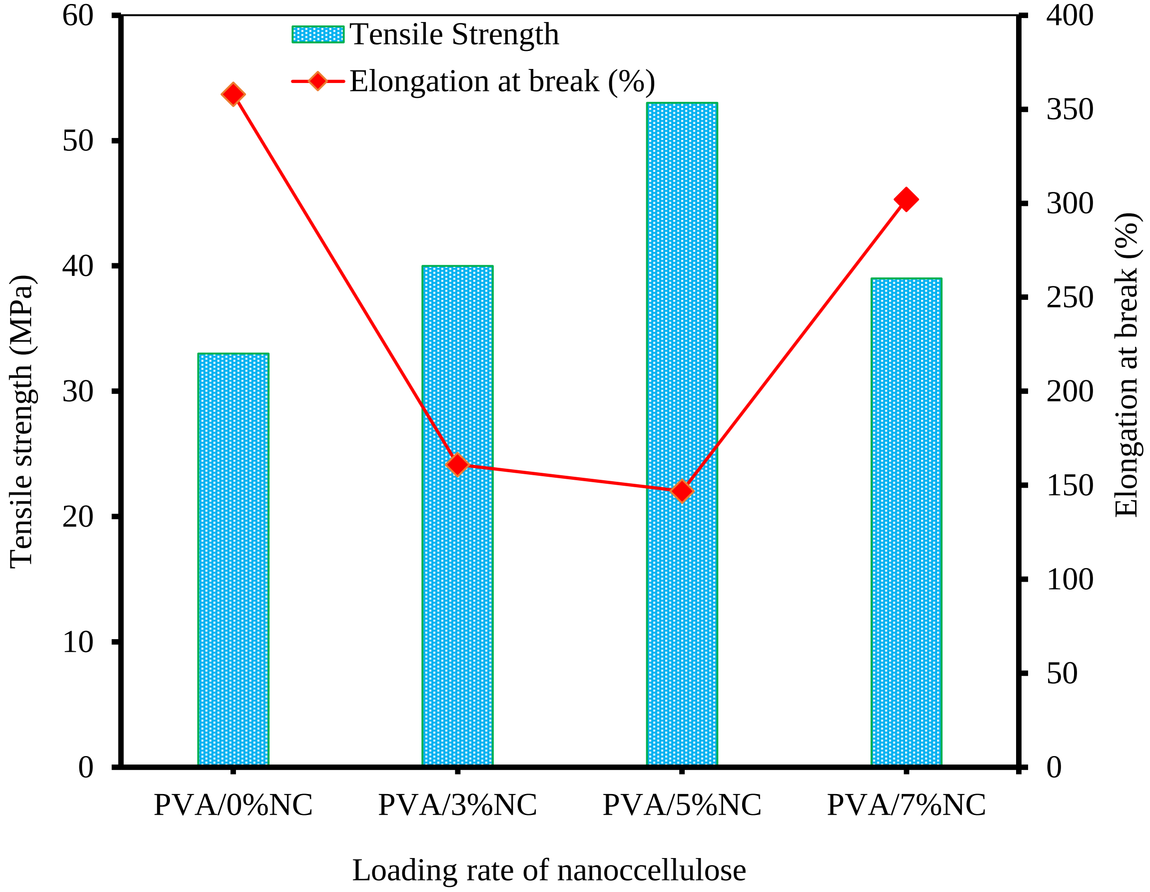

Figure 13 : The tensile strength and elongation at break of the PVA/nanocellulose composite films as a function of the nanocellulose content.

Similarly, when nanocellulose reinforced was compared with bagasse and cellulose reinforced PVA matrix, changes in both tensile strength and elongation at break were observed and given in **figure 14**. For the same amount loading rate of 5 % NC , the nanocellulose reinforced PVA resulted in about 1.5 fold increment with respect to bagasse , 1.4 folds increment with respect to cellulose and 1.6 folds increment with respect to neat PVA. On the other hand, the elongation at break was decreased from 358 (neat PVA) to 329 for PVA/ 5%B, to 306 for PVA/ 5%C and to 147 for PVA/ 5%NC (**figure 14**). Compared to the neat PVA all the reinforcement used were improved both tensile and elongation at break. These results were arisen from high surface area, aspect ratio, high uniform dispersion, tensile strength and young´s modulus of nanocellulose compared to micro level of bagasse and cellulose.

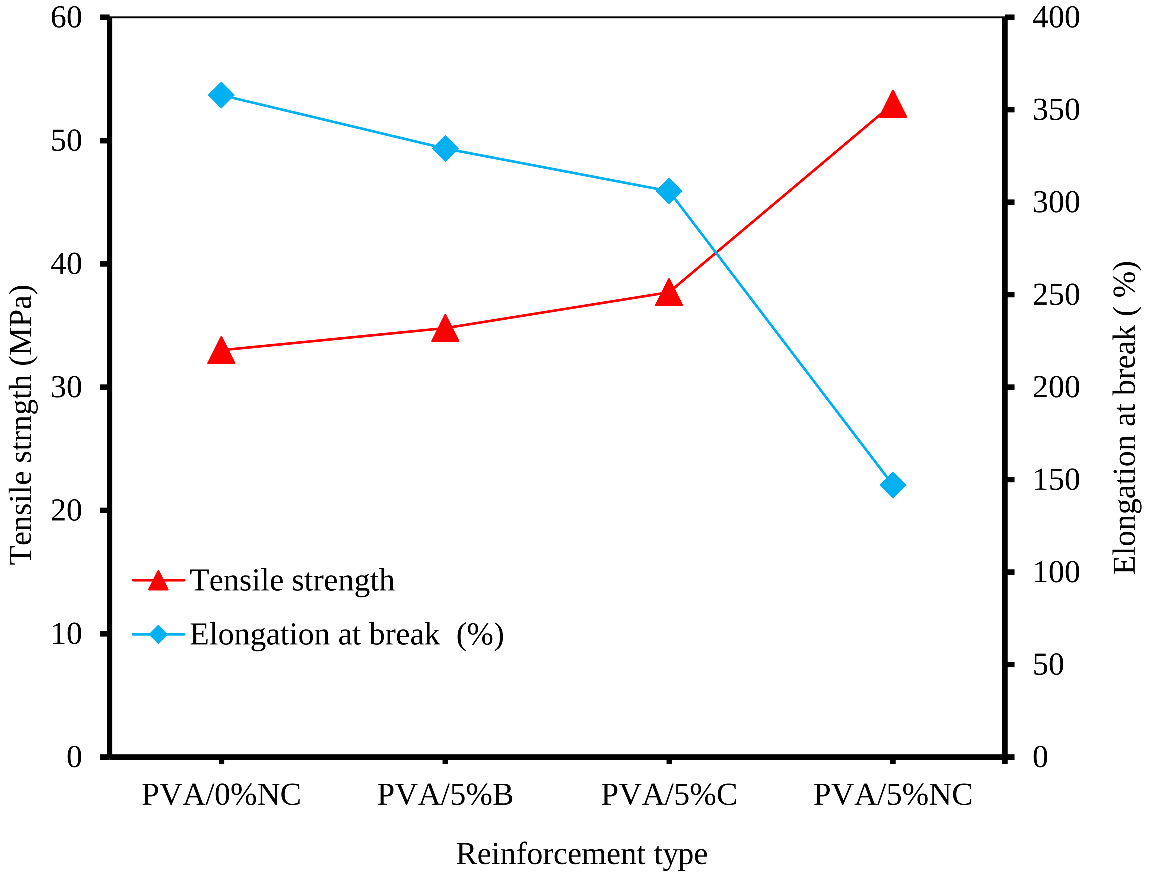

Figure 14: The tensile strength and elongation at break of the PVA/nanocellulose composite films as a function of the reinforcement type.

4.5. Evaluation of effectiveness of reinforcement

In order to evaluate the effectiveness of the reinforcement in PVA polymer matrix, it was important to compare differences achieved between reinforced PVA and neat PVA in terms of their water absorption, mechanical properties and morphology. Thus, the effectiveness of reinforcement was evaluated in terms of improvement in mechanical properties, decrement in water absorption and uniform dispersion of nanocellulose within the host matrix. The results were compared with neat PVA as well as with bagasse and cellulose reinforced PVA films. High surface area, aspect ratio, high tensile strength and young`s modules of nanocellulose are dedicated to improve properties of the matrix and effectiveness of reinforcing ability. The effectiveness of nanocomposite polymer was evaluated in terms of improvement observed in mechanical properties, water absorption and morphology analysis.

4.5.1. Effectiveness evaluation by comparing reinforced PVA with neat PVA

4.5.1.1. Improvement in water absorption

Variations in water absorption were observed between the reinforced and neat PVA samples during the analysis. From the comparative analysis of data presented in **figure 15**, it was possible to demonstrate that the reinforced PVA film resulted in lower water absorption values than the neat PVA film. According to the result, nanocellulose reinforcement applied was effective in lowering the water absorption capacity of the PVA polymer matrix to desired level, which was lower than the water absorption values of neat PVA film.

In other word, the neat film resulted in higher water absorption capacity than the corresponding films that were reinforced with nanocellulose, bagasse fiber and cellulose. These variations were shows that the reinforcement with nanocellulose or fibers reduce water absorption capacity of PVA polymers. This reduction in water absorption capacity shows that polymer matrix that contain nanocellulose and fibers (cellulose and bagasse) have good preventive ability against water. The films that were reinforced with nanocellulose become more water preventive than the neat PVA. This effect indicates the effectiveness of nanocellulose reinforced in PVA polymer matrix in reduction of water absorption capacity. It can be noticed that the presence of nanocellulose in PVA matrix was able to reduce water uptake of the composite, indicating that the nanocellulose was able to increase tortuosity in composite and make the water absorption of the composite to be lowered.

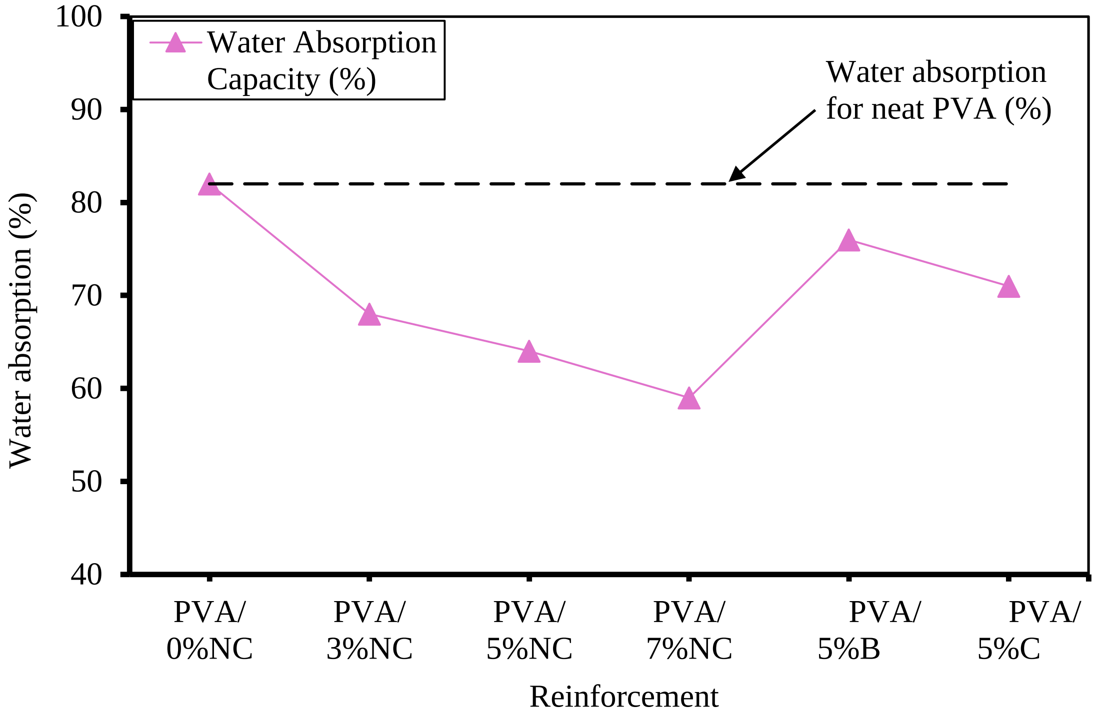

Figure 15: Plot showing comparative analysis of percentage water absorption between nanocellulose reinforced PVA films and neat PVA films.

4.5.1.2. Improvement in mechanical properties

The measured mechanical properties of the reinforced PVA nanocomposites films were exhibited improvement in both tensile strength and elongation at break compared to neat PVA film. The improvement in tensile strength and elongation at break were given in **figure 16** and **17**. Values shown clearly indicate the variation induced on films by the incorporation of nanocellulose in PVA polymer, which resulted in higher tensile strength and lower elongation at break compared to neat PVA film as well as bagasse and cellulose reinforced PVA composite films. These results exhibit that the positive effect brought by incorporating nanocellulose in polymer matrix to increase tensile strength and reduce elongation at break of PVA host matrix. Thus the usage of the nanocellulose produce from sugarcane bagasse for reinforcement application in polymer material was able to improve mechanical properties of the host polymer.

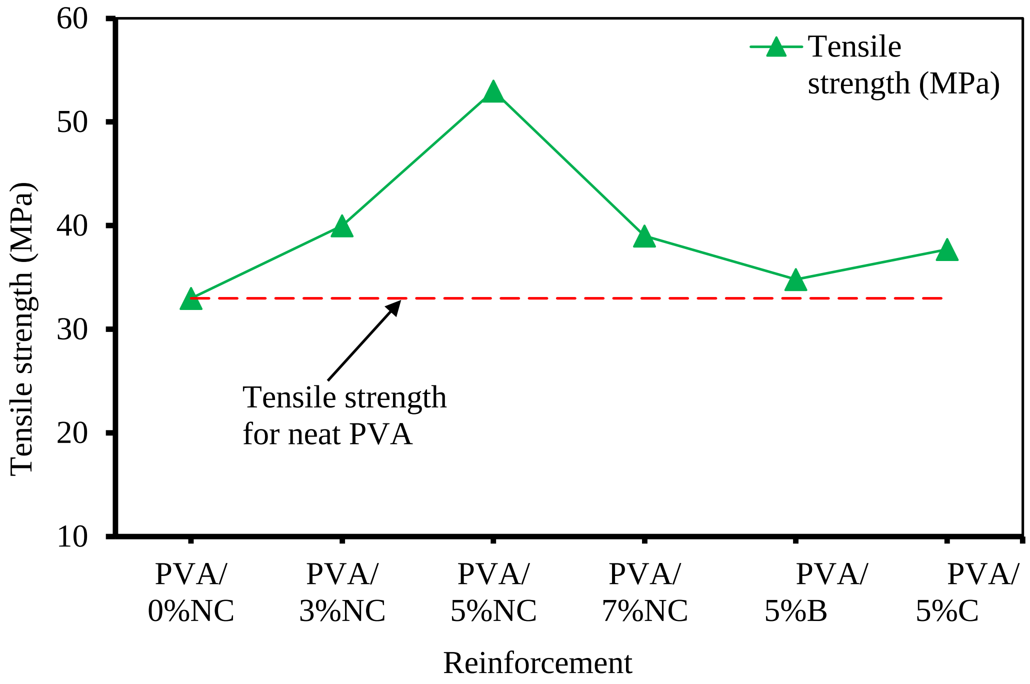

Figure 16: Comparative analysis of tensile strength of PVA composite films and tensile strength of neat PVA film.

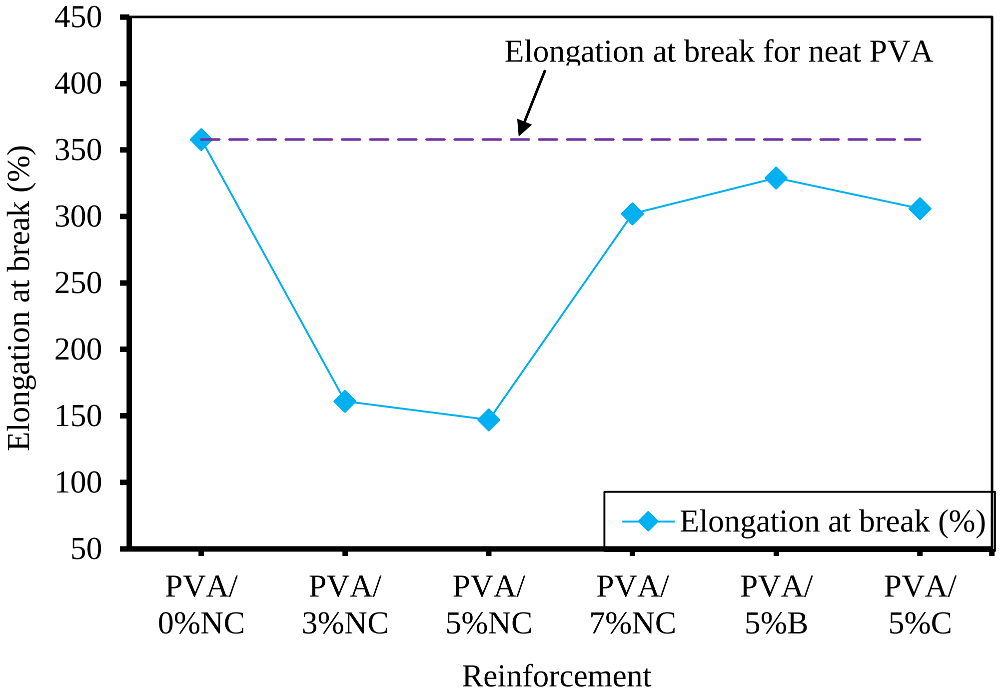

Figure 17: Comparative analysis of elongation at break (%) of PVA composite films and elongation at break of neat PVA film

4.5.2. Effectiveness evaluation by clustering analysis

In order to determine the effectiveness of the reinforcement in production of the PVA composite films in terms of mechanical improvement, water absorption capacity improvement and morphological properties of the PVA matrix, discriminatory analysis based on clustering was done for all the films. By using of this analysis, it was easier to evaluate the effectiveness and efficiency achieved by reinforcement nanocellulose in PVA polymer matrix. Based on the results obtained from water absorption capacity, tensile strength and elongation at break results, clustering was done by categorized into three region: nanocellulose reinforced PVA region, bagasse and cellulose reinforced PVA region and neat PVA region (**figure 18**).

i. **Nanocellulose reinforced PVA region:** this region encompasses the results obtained from nanocellulose reinforced films which exhibited highest tensile strength, lower water absorption capacity and lower elongation at break.
ii. **Bagasse and cellulose reinforced PVA region:** this region covers the results from bagasse and cellulose films that showed lower tensile strength, higher water absorption capacity and higher elongation at break with respect reinforced PVA region.
iii. **Neat PVA region** – this area contains the results from neat PVA films that resulted in lowest tensile strength, highest water absorption capacity and highest elongation at break with respect to reinforced PVA region.

Thus, according to the results obtained from measurements, the PVA polymer that were reinforced with nanocellulose exhibited better results than those reinforced with bagasse and cellulose which in turn much better than those neat PVA films .This revealed that the nanocellulose brought positive effect on the PVA polymer matrix by giving highest tensile strength, lowest water absorption capacity and lowest elongation at break compared to both the neat PVA region , and bagasse and cellulose reinforced PVA region **(figure 18).** Thus, incorporating nanocellulose within polymeric matrix was effective in improving both the mechanical and water absorption capacity of the host matrix.

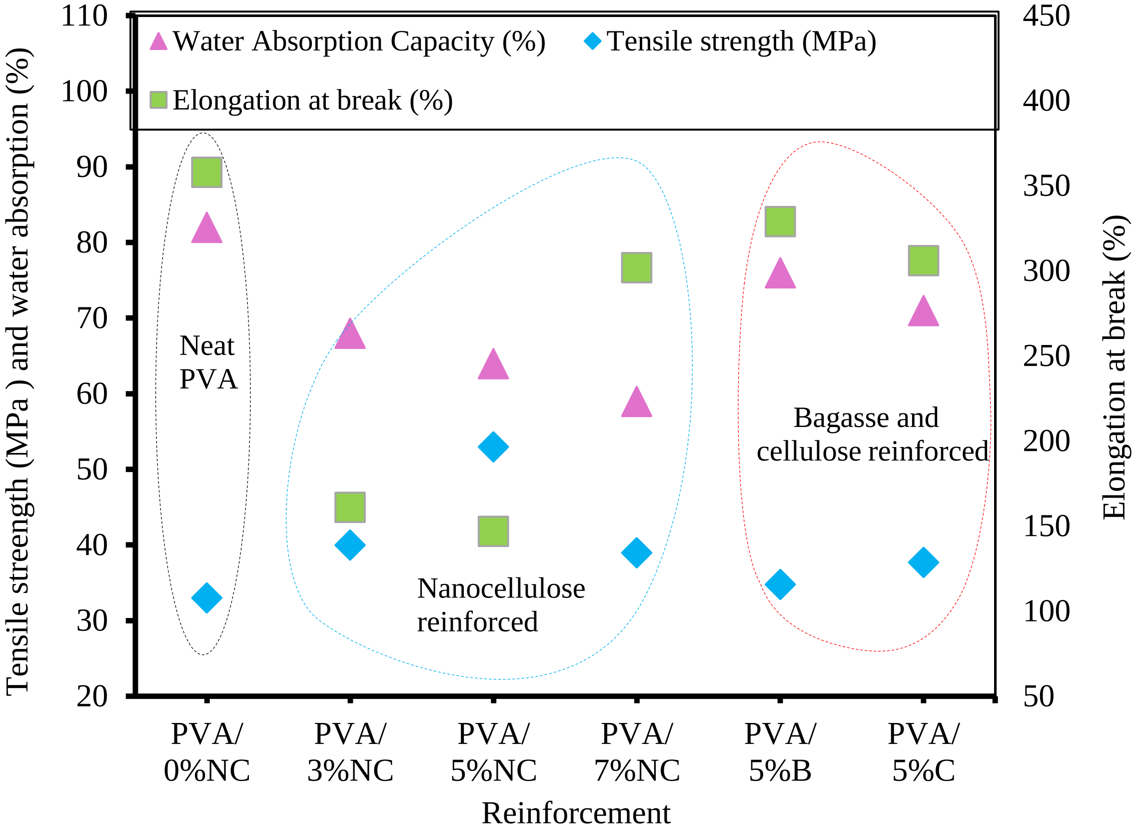

Figure 18: Cluster plot for the reinforced PVA films showing the distribution of the reinforcement values into the three clustered regions.

4.5.3. Effectiveness evaluation with bagasse and cellulose reinforced PVA

The comparative evaluation of nanocellulose reinforced PVA, and bagasse and cellulose reinforced PVA were presented in **figure 19**. The variation in mechanical properties (tensile strength and elongation at break) were observed between nanocellulose reinforced composite films, bagasse reinforced and cellulose reinforced composite films relative to neat PVA film.

For the same loading rate of 5 % NC, the nanocellulose reinforced PVA resulted in about 1.5 fold increment in tensile strength with respect to bagasse reinforced PVA film and 1.4 folds increment in tensile strength with respect to cellulose reinforced PVA film. However, it resulted in about 2 folds of reduction in elongation at break with respect to cellulose reinforced PVA and 2.23 fold of reduction in elongation at break with respect to bagasse reinforced PVA film.

In similar manner, the composite films that were reinforced with nanocellulose showed better results in water absorption capacity than those films that were reinforced with bagasse and cellulose. Higher water absorption was observed in bagasse reinforced PVA relative to the cellulose and nanocellulose reinforced PVA. This was due to higher composition of hemicellulose and lignin in bagasse fiber that exhibited higher water absorption capacity in the bagasse reinforced PVA matrix. Reduction in water absorption capacity for both cellulose reinforced PVA and nanocellulose reinforced PVA films relative to bagasse reinforced PVA arise from the pretreatment used to remove hemicellulose, lignin, relative uniform distribution and the size aspects. This aspects such pretreatment, size and uniform distribution made the composite ability to reduce water absorption. The percentage water absorption capacity of PVA/nanocellulose composite was lower than the bagasse and cellulose reinforced PVA films. This indicates that effectiveness of incorporating nanocellulose in polymers for improving water absorption capacity of host PVA polymer.

The percentage water absorption capacity of PVA/nanocellulose composite was lower and depends on the amount of nanocellulose loading. It can be noticed that the presence of nanocellulose in PVA matrix was able to reduce water uptake of the composite, indicating that the nanocellulose was able to increase tortuosity in composite and make the water absorption of the composite to be lowered.

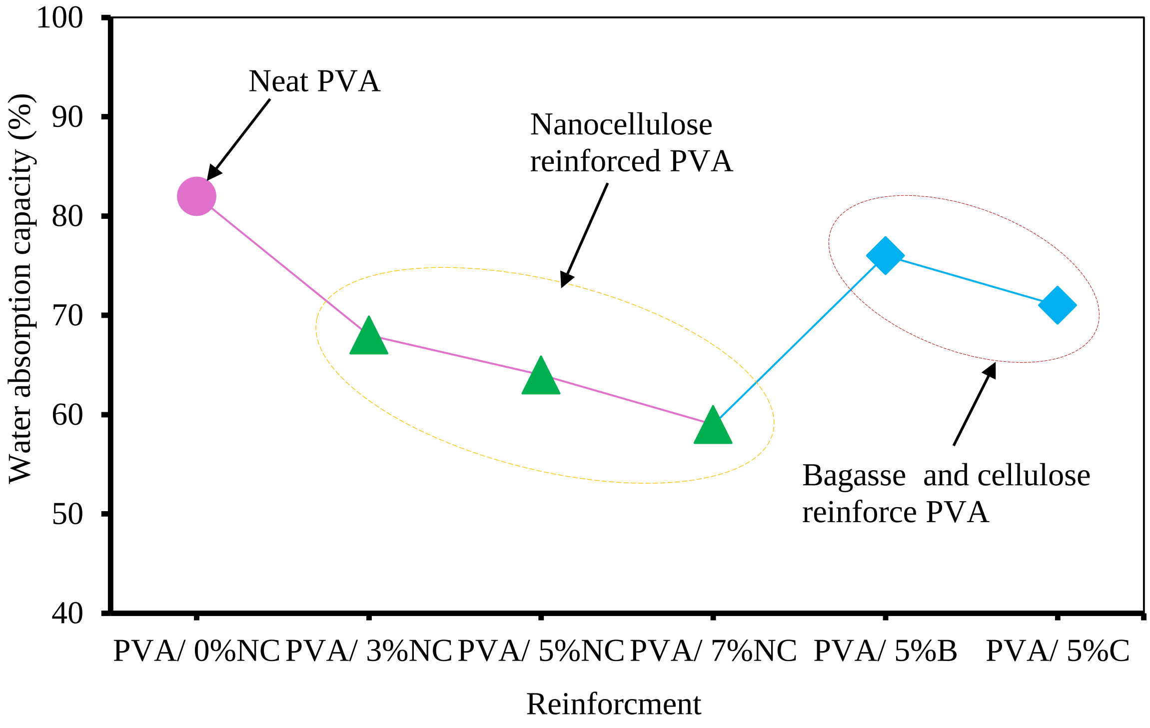

Figure 19: Comparative analysis between nanocellulose reinforced PVA films and bagasse and cellulose reinforced PVA films with respect to neat PVA film.

5. Conclusion

The nanocellulose was successfully extracted from sugarcane bagasse and characterized by dynamic light scattering (DLS) and Fourier transform infrared spectroscopy (FTIR). The particle size analysis by DLS revealed trimodal particle size distribution with corresponding particle size of 80.19 ±17 nm, 442.8 ± 173.4 nm and 5285 ± 416.5 nm . The FTIR result indicated that the effectiveness of used pretreatment in removing lignin and hemicellulose. The reinforced nanocellulose in PVA films with different sets nanocellulose suspension, bagasse and cellulose suspension were produced by solvent casting, and characterized by water absorption capacity, mechanical testing and scanning electron microscopy (SEM).

The comparative and clustering analysis showed that the nanocellulose reinforced PVA films were exhibited significant improvement in water absorption capacity compared to neat PVA, bagasse reinforced and cellulose reinforced PVA films. The water absorption capacity of nanocellulose reinforced PVA films were improved from 82% for neat PVA to 59 % for PVA/7 % NC and to 64 % for PVA/5 % NC composite films. Similarly, for the same amount of reinforcing bagasse, cellulose and nanocellulose in PVA matrix, the nanocellulose reinforced films showed better result in reduction of water absorption capacity. The results clearly showed the effectiveness brought by incorporating the nanocellulose in PVA polymer. This change could arise from size (nanoscale, micro scale), chemical composition (hemicellulose, lignin), interaction between the polymer matrix and the reinforced materials.

The tensile strength and elongation at break results, the nanocellulose reinforced PVA films exhibited highest tensile strength compared to neat PVA as well as compared to cellulose and bagasse reinforced PVA films. The tensile strength was increase from 33 MPa for the neat PVA, to 40 MPa for the 3 % NC, to 53 MPa for 5 % NC and to 39 MPa for 7 % NC reinforcing in PVA polymer. For the same amount reinforcing, the nanocellulose reinforced PVA resulted in about 1.5 fold increment in tensile strength with respect to bagasse, about 1.4 folds increment with respect to cellulose and about 1.6 folds increment with respect to neat PVA. The elongation at break also showed improvement for the nanocellulose/ PVA composite films compared to others and the result was lowered from 358 (neat PVA) to 161 for PVA/ 3% NC, to 147 for PVA/ 5% NC and to 302 for PVA/ 7% NC.

The increment in tensile strength and decrement in elongation at break for the nanocellulose reinforced PVA were resulted from percolation phenomena that improved the mechanical properties of the reinforced composite films.

The SEM micrograph showed that the uniform distribution of nanocellulose in PVA matrix and formation of web like network structure between PVA and nanocellulose by forming rigid percolation reinforced network within host matrix and strong interaction through hydrogen bonding.

The overall results revealed the nanocellulose reinforcement resulted in positive effective both in mechanical and water absorption properties of the host PVA matrix. The cluster and comparative analysis between the nanocelulose reinforced films, bagasse reinforced film, cellulose reinforced film and neat films showed that the nanocellulose reinforced PVA films exhibited highest tensile strength, lower elongation at break and lower water absorption. The bagasse and cellulose reinforced PVA films showed lower tensile strength, higher water absorption capacity and higher elongation at break with respect nanocellulose reinforced PVA but showed higher tensile strength, lower water absorption capacity and lower elongation at break with respect to the neat PVA film. The experimental results from the water absorption, tensile strength, elongation at break and morphology analysis demonstrated that the nanocellulose reinforcement improved the properties of the host PVA polymer.

Recommendation

It is well known that the extraction and reinforcement of nanocellulose from sugarcane bagasse is at infant stage. The Government of Ethiopia has made significant investments in order to boost the production capacity of sugar which in turn increase bagasse production capacity. These efforts have and will continue not only increase production capacity of sugar but also increase the amount of sugarcane bagasse. Abundance of this cellulosic material in Ethiopia and worldwide that can be readily to provide a new area for research development. Therefore, it is recommendable to extract nanocellulose from the bagasse and reinforce in polymeric materials for improving mechanical and water absorption properties. Thesis also open new area for research area based on biomass in our country to convert lignocellulosic biomass to nanocellulose that can be used different application including reinforcing in polymer. Therefore, based on the outcomes of this research work and overall understanding of extraction and reinforcement of nanocellulose in polymeric materials, the following recommendations are stated:

- Further study need to be conducted on optimization of nanocellulose extraction and standard procedure should be produced for the extraction of nanocellulose.
- Further study on determining optimum condition such as acid to cellulose ratio, reaction temperature and hydrolysis time to get best yield using experimental design should be conducted.
- Further study and proposing suitable methods for obtaining nanocellulose crystal should be investigated for the different application.
- Further study on reinforcing nanocellulose in hydrophobic polymers should be investigated.
- It is recommended that other researchers should be done on optimization of nanocellulose extraction using experimental design to increase the product yield
- It is also recommended for researchers to extract nanocellulose from different biomass available in our country and evaluate its effectiveness with other nanocellulose reinforced material.
- It is also recommended to design new way for reinforcing nanocellulose in hydrophobic polymers.

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DECLARATION

I declare that the thesis for the M.Sc. degree at the university of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, that all resources of materials used for this thesis have been duly acknowledged.

Name: **Teshale Tadesse**

Signature: ___________________________

Date of submission: _____________________

This thesis has been submitted for examination with my approval as a university advisor.

Name: **Prof. Belay Woldeyes**

Signature:_____________________________

Date: __________________________