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Obtaining Chitin Nanofibers from Shrimp Shell Waste by High Speed Blender



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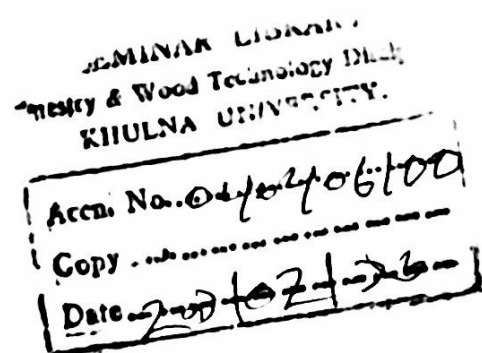
FORESTRY AND WOOD TECHNOLOGY DISCIPLINE
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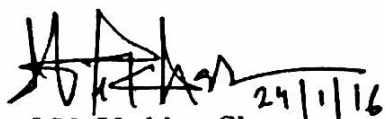
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THESIS WORK

COURSE NO: FWT-5212

This dissertation is submitted to the Forestry and Wood Technology Discipline, School of Life Science, Khulna University in partial fulfillment of the requirements for the award of Master of Science degree

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DECLARATION

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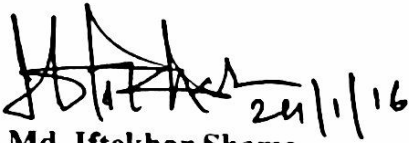
To My

Beloved Parents

Approval

This dissertation has been submitted to the Forestry and Wood Technology Discipline, Khulna University, Khulna, Bangladesh, in Partial fulfillment of the requirements of Master of Science (MS) degree in Forestry. I have approved the style and format of the MS thesis.

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Sourav Bagchi Ratul

ABSTRACT

Chitin nanofibers were successfully prepared from shrimp shell waste using simple blending method under different blending operations. Matrix from shrimp shell was removed by acid and alkali treatment. The pH was maintained 3-4 during preparation of nanofibers. Then, nano-sheets were prepared using vacuum filtering of nanofibers-water suspension. Transparent nanocomposites were prepared by reinforced nanofibers into neat acrylic resin matrix. Characteristics of nanofibers prepared under different blending operation were measured by testing viscosity, dewatering time and precipitation rate of suspensions. It was observed that Mixture of normal and high speed blender showed elevated trend in viscosity (90-95 mPa.s), dewatering time (21 min). Both high speed blender and Mixture showed no precipitation after 2 weeks. The obtained optically transparent nanocomposites present highest 73% of regular light transmittance and 88% of total light transmittance. The lower thermal expansion of nanofibers reinforces composites with high Young's modulus could be prove suitable material for manufacturing different optoelectrical devices.

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1.1 Introduction

In 21st century, nanotechnology holds enormous promising field in research community for generating and revolutionizing materials, systems and devices with a vast range of applications. Usually, nanotechnology deals with stuff sized 1-100 nm in at least one dimension. With the advancement of nanotechnology, fibrillation of nanofibers come under spotlight for their unique characteristics of minute structure, higher surface area, small range of defects and elevated mechanical properties (Ifuku *et al.*, 2011; Yano, 2005). Among the natural polymers, cellulose nanofibers have gained immense attention as reinforcement in nanocomposites (Abe *et al.*, 2007; Nakagaito and Yano, 2005).

After cellulose, chitin is considered to be second most abundant natural polysaccharides occur mainly in the exoskeleton of shellfish (mainly crab and shrimp), some insects and outer cuticles of arthropods (Muzzarelli, 2011). Chitin structure is similar to cellulose with an exception is presence of acetoamide (-NH-CO-CH₃) group in C₂ position instead of hydroxyl group. In addition, chitin is recognized as a biocompatible material with low toxicity, biodegradability, higher crystallinity and hydrophobicity (Shams *et al.*, 2011). High light transmission and foldability makes chitin promising materials for manufacturing optoelectronic devices like solar cells, bendable displays and so on. Recently, several studies were held for successful fabrication of chitin nanofibers from different sources (Shams *et al.*, 2011; Subir *et al.* 2013; Ifuku *et al.*, 2011; Kose and Kondo, 2011). According to Shams and Yano, (2013) optically transparent chitin nanofibers can be fibrillated from crab shell using simplified method. Followed by previous study Subir *et al.* (2013) successfully extracted transparent chitin nanocomposites from shrimp shell wastes. Percot *et al.* (2003) reported that around 10¹⁰ to 10¹² tons of chitin is biosynthesized annually which are discarded from crab and shrimp processing industries without effective utilization. Therefore, it is indispensable to utilize this huge promising biomass resource as an efficient, sustainable and environment friendly material.

Bangladesh is plentiful of shrimp production and comprises enormous number of shrimp processing industries in the coastal region of the country. These industries process 265000 metric tons of shrimp per year (Haq *et al.*, 2009). Head and body carapace of shrimp comprise 48-56% of body parts (Sachindra *et al.*, 2005). So, around 138000 metric tons of shrimp waste are produced annually by these processing industries. Most of the wastes are discarded and very few are used for processing low valued fish feed and fertilizer. This huge amount of

unprocessed waste cause great extent of environmental pollution in present and will be expand in future (Islam *et al.*, 2004). Like developed countries, this huge waste can be utilized to fabricate and develop high valued chitin nanofibers and subsequently to transparent nanocomposites. Considering these things, Subir *et al.* (2013) firstly made an attempt to prepare chitin nanofibers from shrimp shell wastage under acidic and non-acidic condition. Hence, the purpose of this study was to obtaining chitin nanofibers from shrimp shell wastage using different blending operations.

1.2 Objectives

- α To prepare chitin nanofibers from shrimp shell wastage using high speed blender.
- α To fabricate transparent low thermal expanded film from those nanofibers.

2.0 Literature Review

2.1. Chitin and its structure

Chitin can be found in animals, in exoskeleton shells of arthropods (crabs, shrimps and beetles), internal flexible backbone of cephalopods, worms, webs of spiders, cell walls of fungi and mushrooms (Chen *et al.*, 2008). It is a high molecular weight and linear amino-polysaccharide known to be made of 2-acetamido-2-deoxy- β -D- glucopyranose through a $\beta(1\rightarrow 4)$ linked structure (Ifuku *et al.*, 2009). The $\beta(1\rightarrow 4)$ -N-acetyl glycosaminoglycan structure with two hydroxyl groups and an acetamide group makes chitin very crystalline with strong hydrogen bonding (Lertwattanaseri *et al.*, 2009).

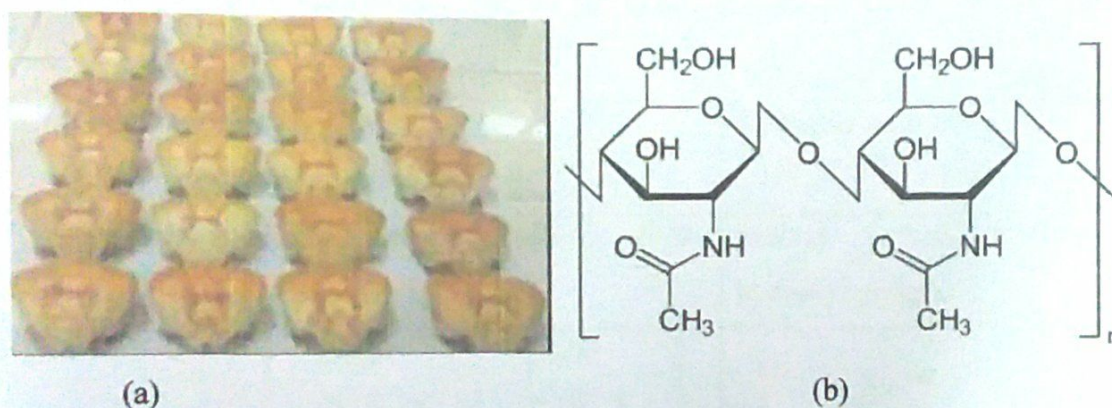


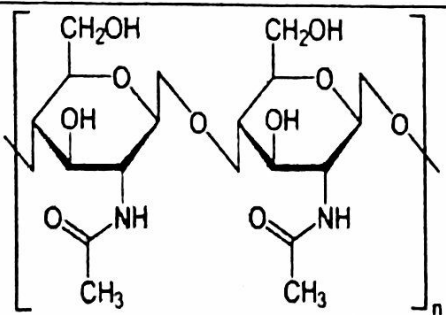
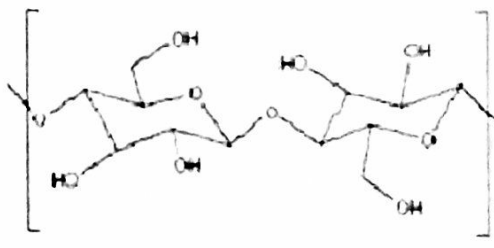
Figure 2.1 (a) Crab shell, (b) Chitin molecular structure

Chitin is a semi-crystalline biopolymer which forms microfibrillar arrangements in living organisms. Native chitin fibers are made up of thin filaments, crystalline fibrils called microfibrils, tightly bonded to each other through a large number of hydrogen bonds (Mincea *et al.*, 2012). The chitin microfibrils consist of nanofibers about 2–5 nm in diameter and about 300 nm in length embedded in several protein matrices (Raabe *et al.*, 2012). Since these fibrils are typically embedded in a protein matrix and their diameters range from 2.5 to 2.8 nm, depending on their biological origins [48]. But in mushrooms cell the chitin nanofiber is embedded in glucans matrices [54, 55]. The width of the nanofibers depended on the type of mushrooms and varied in the range 20 to 28 nm. Chitin microfibrils are constituted of alternating crystalline and amorphous domains [36]. Chitin is predominantly present as a fibrillar crystalline material. Native chitin can occur in one of the three crystalline forms [49]: α -chitin, β -chitin, and γ -chitin, respectively, depending on its origin.

2.2 Comparison between chitin nanofiber and cellulose nanofiber

There is a growing interest in producing nanofibers from natural polymers where cellulose is the first abandoned natural source of nanofibers and chitin is second. Cellulose is selected for nanofibers extraction for its special features as crystalline structure of microfibrils, Young's modulus is 138 GPa [68], their tensile strength is at least 2 GPa and their thermal-expansion coefficient in the axial direction is as small as 0.1 ppm/K [69] that's is helpful for process regulating. Similar to wood cell walls, the exoskeletons of crab and prawn have a strictly hierarchical structure consisting of crystalline α -chitin nanofibers embedded in matrix components [70] and the quality of nanofibers is better than cellulose nanofibers. There is made comparison between chitin and cellulose given below-

Table -2.1: Important comparison between chitin and cellulose

Name of the feature	Chitin nanofiber	Cellulose nanofiber
1. Chemical Structure	Second carbon molecule holds acetamide group.	Second carbon molecule holds hydroxyl groups.
2. Figure		
3. Related Matrices	Chitin microfibrile embedded into the protein material and closely associated with proteins, minerals, lipids and pigments [62].	Cellulose microfibrile embedded in hemicelluloses and lignin.
4. Filtering speed	Greater than cellulose nanofibers [63].	Greater than normal paper but less than chitin nano fibers [63].
5. Purification method	Removing of matrix from shells is easy [66].	Removing of hemicelluloses is difficult [65].
6. Transparency	Higher [67].	Lower then chitin.

2.3 Extraction of chitin nanofibers

Chitin nanofibers have been extracted from crab shells having such complicated hierarchical structures [46]. The molecules are aligned in an antiparallel manner that gives rise to α -chitin crystals in the form of thinner nanofibers. The production method of the present invention of chitin nanofibers are thin, homogeneous and long, and also have molecules composed of an extended chain crystalline structure and have a high strength[73]. The obtained nanofibers were observed by FE-SEM and found to have a uniform width of approximately 20-40nm and high aspect ratio that more than 1000. The exoskeletons of crabs and prawn are made up of two parts, the exocuticle and endocuticle where exocuticle has a fine twisted plywood structure and endocuticle has a thicker and coarser structure [18]. Crab shells are made up of the coarser endocuticle [47] and prawn shells are made up of a finer exocuticle[74]. As result of this finer structure nano-fibrillation of prawn shell is easy, which allows chitin nanofibers to be prepared under neutral pH conditions than crab shell. To extract chitin nanofibers from crab shell or prawn or mushrooms the samples were purified by a series of chemical treatments. A very recently developed [75] Star Burst atomization system which employed high pressure water jet system where slurry of chitin in high acetic acid medium is introduced in chamber of Star Burst system machine where it is fibrillated into NFs of width (18.0-19.0 nm). The two other commonly used apparatus used for fibrillation are a blender and grinder.

2.3.1. Chemical treatment

2.3.1.1 Prawn shell

To extract the chitin component from the prawn shell, proteins and minerals were removed according to the conventional method using aqueous KOH, NaClO and HCl [80]. The pigment component in the sample was then removed using ethanol. The yield of dry chitin from the wet prawn shells was approximately 16.7% [85]. The degree of deacetylation (DDA) of the samples determined by the C and N content in the elemental analysis data was 7%. [82]. Procedure is described in below according to the flow chart.

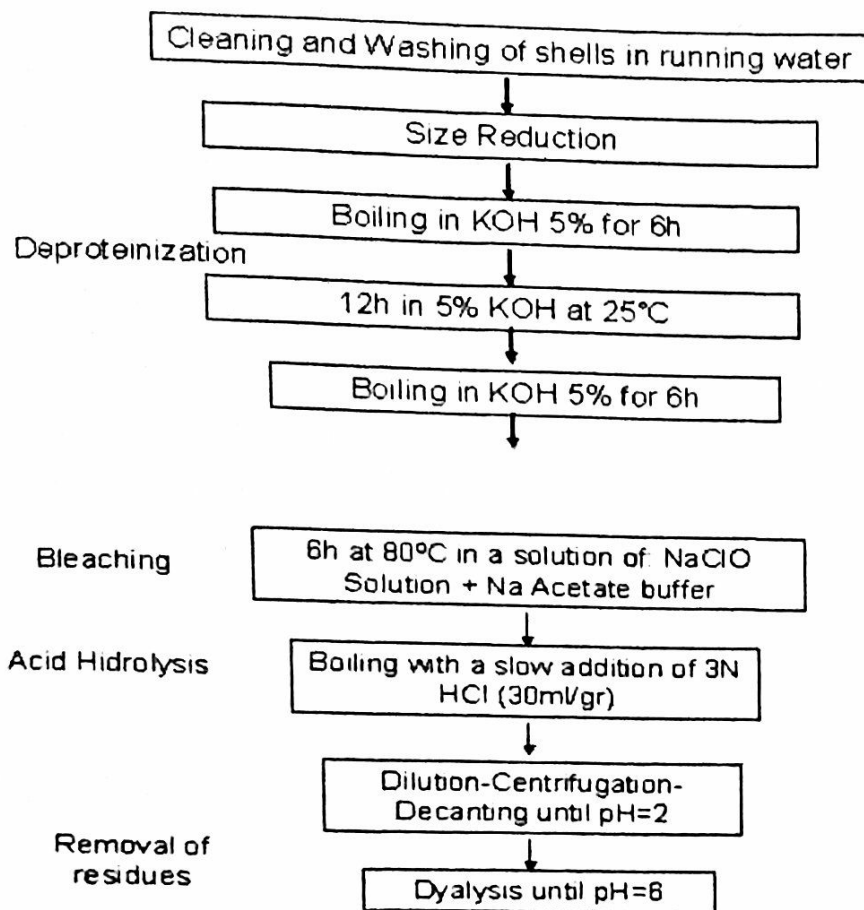


Figure 2.2: Scheme of mechanical and chemical treatments applied to shrimp shell to obtain chitin

2.3.2 Mechanical fibrillation of Chitin

Purified dry chitin was dispersed in water at 1 wt% and dissolved in pH 3 acidic water by adding acetic acid to facilitate fibrillation [92]. The mixture was stirred at room temperature over night. Slurry was vacuum filtered to obtain wet chitin cake. Chitin cake was dissolved in water again, acetic acid was added to level a pH 3[92]. This chitin-water slurry was ready for fibrillation in mechanical grinder. The chitin was roughly crushed with a domestic blender. The slurry was passed through a grinder at 1500 rpm [70]. The fiber width was 25 - 40 nm [92].

2.3.3 Star Burst system for chitin fibrillation

Star Burst system (SBS) developed a new way to prepare NFs from commercially available dry α -chitin powder from crab shell with and without acetic acid medium [93]. It's have a chamber where high pressure water jet system is used to fibrilized the slurry of chitin [199]. Atomization occurred in this newly developed machine chamber by collision to ceramic ball

that throws out fine fibrillated NFs at extremely high pressure of 245 MPa through an out let nozzle [23]. Fibers were thinner in acidic medium than neutral conditions. NFs prepared in SBS were thinner than grinder treatment in acidic medium [95]. To decrease the length of fiber above 30 passes of high pressure are required. The mechanical properties are improved by the number of passes up to 30.

Under neutral condition the chitin was not fibrillated in one pass (Fig. (a))[93]. Thick aggregates of CNFs were observed. There was a significant change in the morphology of CFs after the treatment with five and ten passes (Fig. b, c, d, and e) [93]. The width of fibers in five passes is 18.2 and it reduced to 17.3 nm in ten passes. Thus SBS is powerful tools to give fibers of very thin diameter even without acetic acid solution pool.

If we consider the atomization of CNFs in SBS with acetic acid and observed the fiber length according to one, five, and ten passes are 19.0, 18.0, and 16.5 nm, respectively [93]. It is very noteworthy that advantage of very recently developed advanced technology high pressure jet SBS can atomized chitin slurry with or without acetic acid in just five passes to give NFs of small diameter (18.0-18.2 nm) and with high aspect ratio [199]. The decreasing of the width of nanofibers is happened with the increasing number of passes. After the Star Burst process under both acidic and neutral conditions, there was no significant difference in the relative degree of crystallinity after the various numbers of passes [95].

3.0 Materials and Methods

3.1 Materials

Shrimp shell was used as main source of chitin nanofibers and obtained from Rupsha Sea food Industries Ltd. Hydrochloric Acid (HCl), Sodium Hydroxide (NaOH) and Ethanol was used for eradicating matrix. A normal blender (Panasonic) and a high speed blender (Vita-Mix blender) were used to fabricate the chitin nanofibers. During this fabrication Acetic acid was used to facilitate the fibrillation of nanofibers. Finally, Neat Acrylic resin was used to convert the semi transparent nanocomposites into a transparent one.

3.2 Preparation of Chitin Nanofibers

The shell of shrimp was washed and air dried for three days. The dried shell was then treated with different chemicals as the shell contains matrix substance like proteins, lipids, calcium carbonates and pigments. Initially blended shell powder was treated with 7% HCl solution for 24 hours at room temperature to remove calcium carbonates. After 24 hours, the sample was filtered and rinsed with an abundance of distilled water for neutralization of mineral salts residues. This action was repeated two times for ensuring complete removal of mineral salts. After this, deproteinization of sample was done through 4% NaOH treatment for 4 hours at 60°C temperature and kept under vigorous stirring for 20 hours at room temperature. Later than, the sample was again filtered and rinsed with nonstop distilled water flow. The whole procedure also repeated two times in favor of completing proteins removal. Pigment removal from sample was done through 50 wt% ethanol for 12 hours at room temperature. The yield of chitin after chemical treatments was estimated around 14.3 wt%.

The purified wet sample (chitin) was dispersed in distilled water with a concentration of 1 wt% forming slurry. The slurry was then stirred for 6 hours and several drops of acetic acid were added into the slurry to reduce the pH value between 3-4 ranges. This addition of acetic acid into slurry facilitates the fibrillation and homogeneous dispersion of chitin nanofibers. Afterward, four different types of suspension were prepared on basis of blending operation such as normal blender (4000 rpm) for 10 minutes, high speed blender (37000 rpm) for 10 minutes and mixture of normal and high speed blender for 10 and 20 minutes. All of them were kept in a never-dried condition.

3.3 Preparation of Chitin Nano-sheets

The fibrillated chitin nanofibers were neutralized and dispersed into distilled water at 0.1 wt% of nanofiber contents. These suspensions were stirred for 6 hours. After stirring, 260 g of water suspension was vacuum-filtered through PPTe membrane filter (0.2 μ m) to produce a wet nano-sheet of 90 mm in diameter. The wet chitin sheet was separated firstly from the filter paper and dried at 103 \pm 2 $^{\circ}$ C and 2N/mm² pressure for 6 minutes. The thicknesses of nano-sheets were varied between 30 to 60 μ m.

3.4 Preparation of Chitin-plastic Nanocomposites

The dried nano-sheets were impregnated with neat acrylic resin A-BPE-10 matrix (refractive index 1.537) and vacuumed for 12 hours at a reduced pressure of 0.08 mPa. After reinforced of nano-sheets into resin matrix, the impregnated composites were cured using ultraviolet light. The chitin/resin composites thicknesses were approximately between 100 to 120 μ m. The fiber content of chitin reinforced nanocomposites were 23-27 wt% which was obtained by the oven-dry weight of chitin nano-sheet and chitin-plastic nanocomposite.

3.5 Viscosity

Viscosity was tested by VTE-03 viscometer using number 3 rotor. Four suspensions of 460gm of chitin slurry were prepared based on different blending operations.

3.6 FE-SEM Observations

The chitin nano sheets were coated with an approximately 2 nm layer of platinum by an ion-sputter coater and observed with a field emission scanning electron microscope (JSM-1600F, JEOL Ltd.).

3.7 Light Transmittance

The regular and total light transmittances of chitin/resin composites were measured using a UV-visible spectrometer (U-4100, Hitachi High-Tech. Corp.) with an integrating sphere 60 mm in diameter at wavelengths from 200 to 1000 nm. Transmittance was measured by placing the specimens 25 cm from the entrance port of the integrating sphere.

3.8 Coefficient of Thermal Expansion

CTE were measured by a thermo mechanical analyzer (TMA/SS6100, SII Nanotechnology Inc. Specimens were 25 mm long, 3 mm wide and 100-110 μm thick with a 20mm span.

4.0 Results and Discussion

4.1 Characterization of Chitin Nanofibers

Shrimp shell contains strictly hierarchical organization of several substances. The anti parallel alignment of chitin molecules leads the alpha chitin crystals into chitin nanofibers having diameter of 2-5 nm (Shams and Yano, 2013). These chitin nanofibers are huddled into chitin/protein fibers of 50-300 nm in diameters and surrounded by array of protein and minerals (Raabe *et al.*, 2005). The shrimp shell was treated with acid an alkali in order to demineralization and deproteinization for isolating chitin nanofibers. Removal of these residues turned the shrimp shells into semi transparent soft chitin (Figure 4.1a). The yield of chitin was estimated 14.3 %. After that, the chitin was kept in a wet condition by forming 1 wt% suspension. The pH value to 3-4 was maintained by adding several drops of organic acid and stirred for 6 hours to ensure homogeneous dispersion of chitin fibers. Therefore, four types blending operations were done to facilitate the fibrillation. During chemical treatment, some acetoamide groups ($-\text{NH}-\text{CO}-\text{CH}_3$) at C_2 position of chitin molecules are converted into deacetylated amino groups ($-\text{NH}_2$). In acidic condition, these amino groups ($-\text{NH}_2$) converts into positive charges ($-\text{NH}_3^+$) on nanofibers surface which create an inter-fibrillar electrostatic repulsion force in water (Shams *et al.*, 2011). This force breaks the strong hydrogen bond between the nanofibers and ensures homogenous dispersion of nanofibers (Figure 4.1b).



Figure 4.1. a) Semi transparent shrimp shell after chemical treatment. b) Microscopic view ($\times 40$) showing homogenous dispersion of chitin nanofibers in acidic condition.

4.2 Precipitation Rate of Suspension

Suspensions of 1 wt% chitin having different blending operations were kept in four test tubes to measure the degree of fibrillation. Precipitation rate of normal blended (rotation 4000 rpm)

slurry was observed very fast while precipitation rate of high speed blender and mixture slurry was remaining unchanged after two weeks (Figure 4.2). This occurred because of obtaining colloidal structure after 15,000 rpm rotating speed as demonstrated by Shams and Yano (2013).

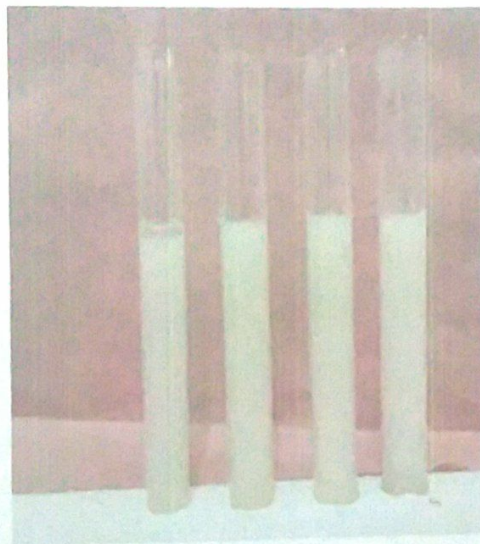


Figure 4.2 Suspensions of nanofibers at different blending operations.

4.3 Viscosity

Viscosity was increased with the rotation speed associate with different blending operation. Figure 4.3 explains that 1wt% chitin slurry prepared by normal and high speed blender mixture showed greater viscosity while normal blender showed lowest viscosity. The viscosity differs with the morphological characteristics of nanofibers. Thinner and shorter fibers can intertwine more frequently than long fibers. According to this statement it can be say that, 20 minutes mixture blending can ensure shorter and thinner nanofibers with homogeneous fibrillation.

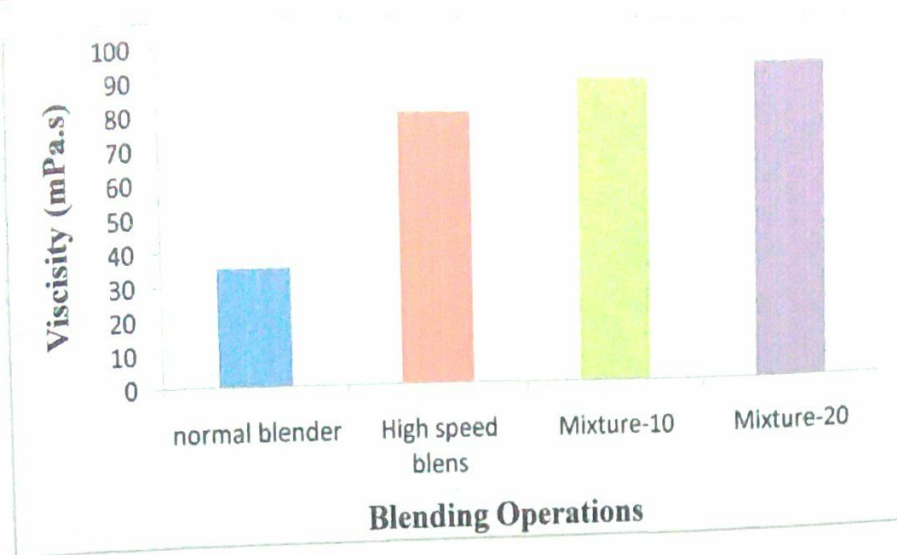


Figure 4.3 Viscosity variations between slurries of different blending operation.

4.4 Dewatering Time

The effect of different blending operations on the suspension was determined indirectly through the dewatering time of suspension. Firstly, fibrillated chitin was dispersed into water at a concentration of 0.1wt% and total 260g of water suspension was vacuum filtered during production of chitin nano-sheets. The effect of blending operation on dewatering time was presented in figure 4.4 where 20 minutes mixture blending took highest minutes than others. This might happened due to shortening of nanofibers and increasing of surface area since dewatering time is related to the surface area. Though, all the suspensions show lower trend of dewatering time in contrast with cellulose nanofibers.

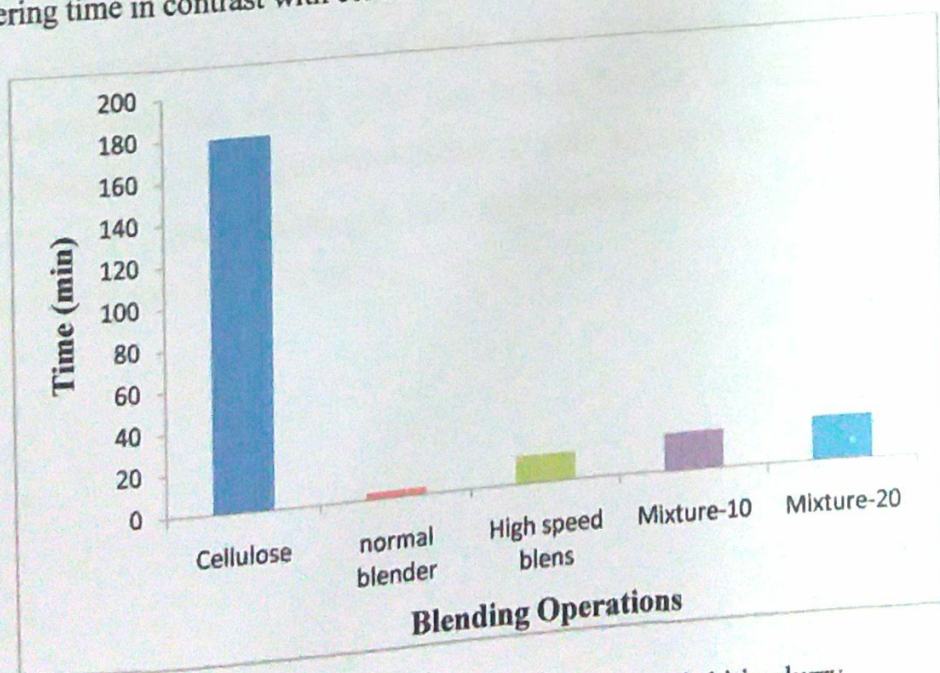


Figure 4.4 The effect of blending operation on filtration time of chitin slurry.

4.5 Microscopic and FE-SEM Image

To understand the fibrillation, firstly microscopic images were observed (Figure 4.5a). From microscopic view, it was clearly observed the difference between normal blander and others. The fibers were not fibrillated properly and showed bundle of fibers in normal blended sheet. 20 minutes mixture showed more homogeneous dispersion of fibers and barely seen any fibers bundle in microscopic view. There is no visual difference present between high speed and 10 minutes mixture in microscopic view. For understanding their difference clearly high magnification FE-SEM image were observed. The FE-SEM image if high speed blander shows that a well constructed chitin nanofibers having uniform width of 40-50 nm were fabricated (Figure 4.5b). The dark spots in microscopic images are describing presence of pigments. The pigments may remain for poor washing with water during chemical treatments.

4.6 Optical transparent Chitin Nano-sheets

The chitin nano-sheets were impregnated into neat acrylic resin matrix to produce optically transparent chitin nanocomposites. Figure 4.6 shows that optically transparent nanocomposites could be produced by nanofiber reinforced acrylic resin films.

4.7 Light Transmittance

Figure 4.7 shows the regular and total light transmittance against wavelength measurements for the chitin reinforced composites and pure acrylic resin sheets. According to the graph, 10 minutes mixture shows 73% transmittance were 20 minutes mixture shows lower transmittance (55%) than others. This was happed because of high pigment materials presence. Compare to the light transmittance of pure acrylic resin (90.5%), the network degrade 17% of the light transmittance. But total transmittance graph presents no differences at 800 nm wave length (Figure 4.7b).

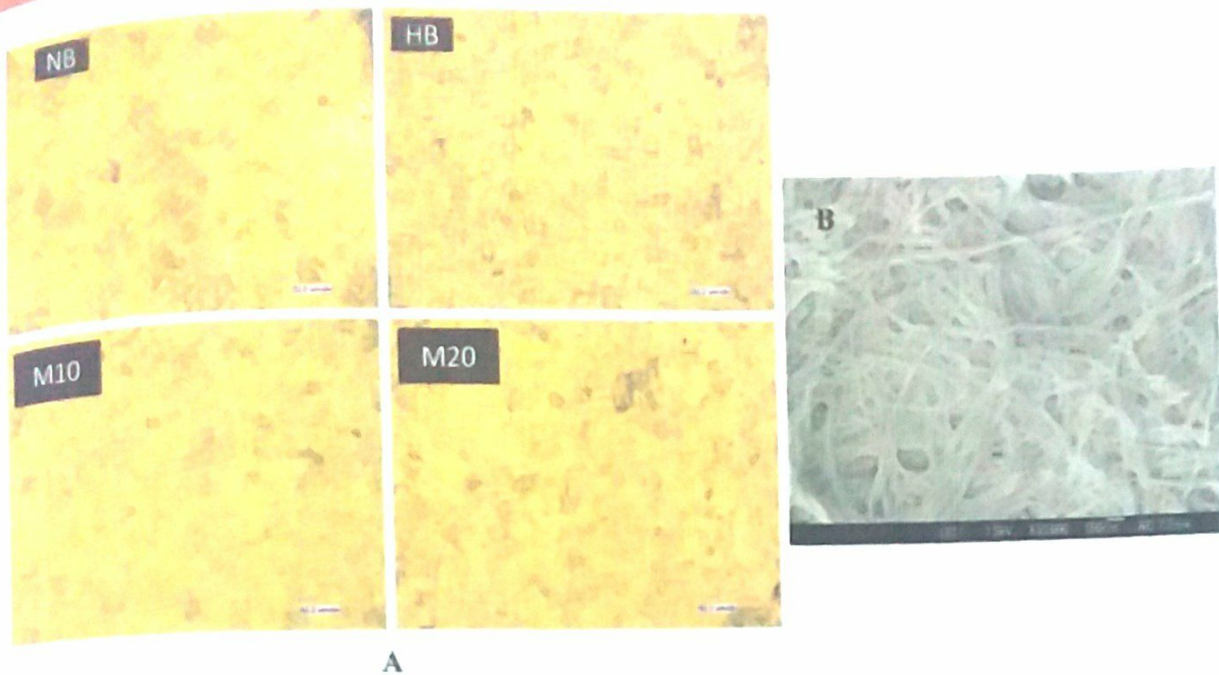


Figure 4.5 a) Microscopic view ($\times 100$) of chitin nano-sheets. b) FE-SEM image of high speed blended nano-sheet.



Figure 4.6 Optically transparent chitin nanofibers reinforced acrylic resin sheet.

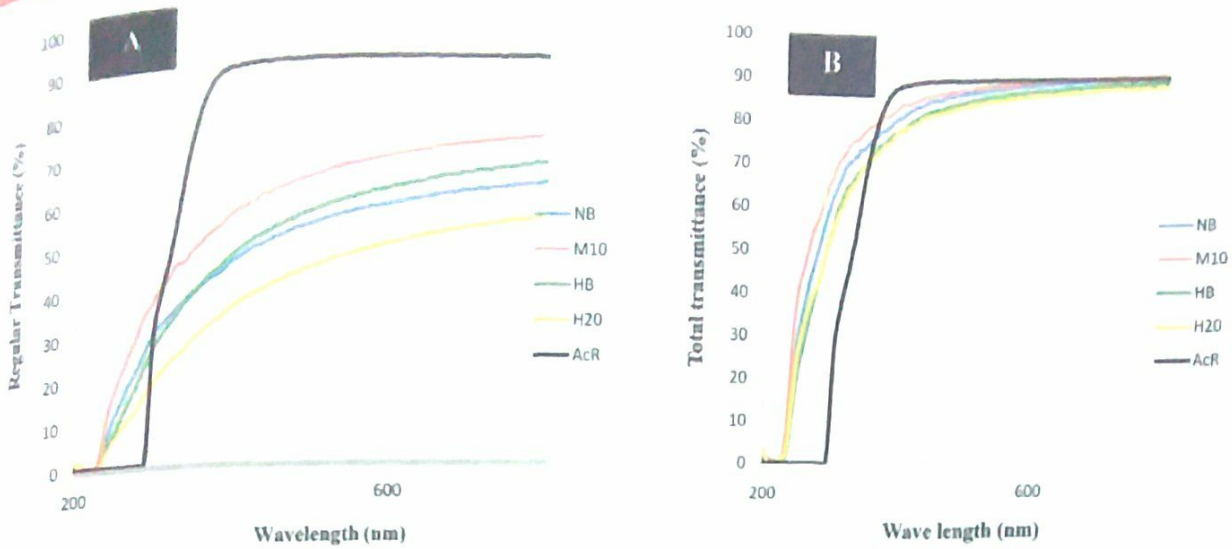


Figure 4.7 Regular light transmittance (a) and Total light transmittance (b) of chitin/resin nanocomposites.

4.8 Coefficient of Thermal Expansion

Figure 4.8 presents reduction of thermal expansion than pure acrylic resin film. High speed blender and mixture shows lower thermal expansion than normal blender. But the thermal expansion of chitin reinforced nanocomposites show higher thermal expansion compare with the previous studies (Shams and Yano, 2013). This happened due to poor entrance of acrylic resin into nanofibers network. This poor entrance might be the cause of high pigment materials presence. Thermal expansion is inversely related to the Young's modulus. Lower thermal expansion indicates higher Young's modulus of chitin/resin nanocomposites.

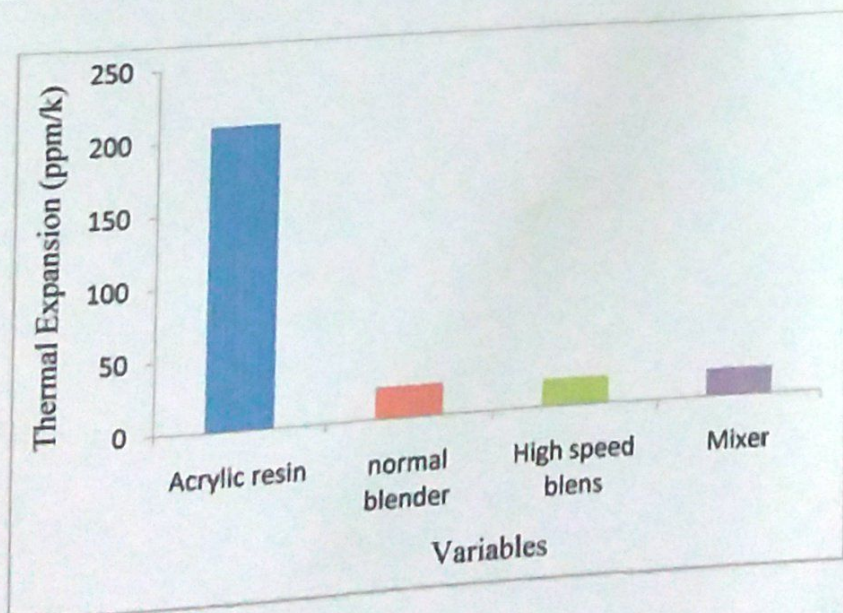


Figure 4.8 CTE of fibrillated composite films as a function of different blending operations.

5.0 Conclusion

From the detailed analysis of data and on the basis of outcome following specific conclusion can be made:

1. Nanofibers fibrillation can be done by simple mechanical process from shrimp shell wastage.
2. Different blending operations have greater effect on the homogeneous fibrillation of nanofibers.
3. Optically transparent nanocomposites can be produced by reinforcement nanofibers into acrylic resin matrix. Nanocomposites show high light transmittance and lower thermal expansion.

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