Development of Flexible and Optically Transparent Composite Film with Wheat Straw Nanofibres

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science in Forestry
Faculty of Forestry
University of Toronto

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Abstract

Cellulose is a potential source of nano-material not only because it possesses excellent mechanical and optical properties, but also because it is environmentally benign. In this study, nanofibres derived from wheat straw, an agriculture residue, was utilized in producing flexible and optically transparent nanocomposite films. The composites were produced using a bi-phase impregnation technique that coats the dried nanofibre films with clear polyurethane acrylate resins using UV radiation induced curing. The nanocomposite films thus produced possess excellent tensile properties (161MPa in strength and 9GPa in Young’s Modulus), superior thermal stability (above 300°C), low coefficient of thermal expansion (8-9ppm/K), good light transparency (80%), excellent flexibility and abrasion resistance. These nanocomposite films are aimed to replace the conventional glass substrates made in batches to a polymer based substrates that can be efficiently produced in a roll-to-roll process for the base of the future flexible flat panel displays.
Acknowledgement

This research project would not have been possible without the encouragement and support of many individuals.

Foremost, I owe my deepest gratitude to my supervisor, Professor Mohini Sain, for his inspiration, trust, invaluable advices and support. I am very thankful to the members of my supervisory committee, Dr. D.N. Roy and Professor Sally Krigstin for their knowledge and encouragement along the way. Without them, I would not have started my master degree at the first place.

Special thanks also goes to everyone at the Faculty of Forestry, especially to Lynn and Shiang for their tremendous help and sharing of knowledge. I am indebted to many of the professionals outside of the faculty who have provided me assistance during the course of my study. Sincere gratitude is due to George at Department of Geology, Lindsey and Nana at Department of Chemistry, Sarute and Professor Hathaikarn at Chulalongkorn University, Subrata at Canadian General Tower, Magdalena and Dawn at GE Power and Water.

I would like to convey my gratitude to the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) for providing financial support.

Finally, I wish to express my thankfulness to my parents, Yang and my friends for their unconditional love and understanding ever since.
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Chapter 1  Introduction

Since its first introduction in 1959, nanotechnology, which is the study of materials on a molecular scale, has advanced progressively and changed our lives in a profound way with numerous applications in many different areas. Cellulose is a potential source of nano-material not only because it possesses excellent mechanical and optical properties, but also because it is environmentally benign. Recently, cellulosic nano-structures have received a lot of attention for its potential application in novel cellulose-reinforced composite product, and are currently considered one of the most promising materials for scientific and technological advancement.

Defined by Wegner and Jones (2006), nano-scaled cellulosic structures usually measure 100 nm or less in at least one dimension. 100nm preferably refers to the diameter. Cellulose nano-structures are one of the fundamental structural building blocks of plants and some animals, but they are often embedded in a complex matrix that hinders their straightforward usages and applications in a number of processes. In other words, cellulose nano-structures do not exist in their pure form. Latest technological advancements allow cellulose nano-structures to be isolated from wood, agricultural residues and marine animals, or cultivated from specific strains of bacteria (Hubbe et al. 2008). The selection of the isolation process depends heavily on the form of the cellulose nano-structure desired. Cellulose is a polysaccharide chain consisting of β-1,4 linked D-glucose units. These glucose units are either arranged in an orderly and dense manner or a random and loose manner known as crystalline region and amorphous region, respectively. These two regions alternate along the cellulose chain and the latter is more susceptible to chemical and mechanical disturbance. Depending on the integrity of the amorphous region, cellulose nano-structures can be categorized into two types, cellulose nanowhiskers (purely crystalline) and cellulose nanofibres (combined crystalline and amorphous) (Sain and Oksman 2006). These aforementioned forms are both optically transparent as their diameters are much less than the wavelength of visible light, but cellulose
nanofibres have more reinforcing ability given credit to their high aspect ratio (Novak 1993).

In terms of single fibre properties, cellulose nanofibres are reported to have Young's modulus close to near-perfect cellulose crystals (138 GPa), and an estimated tensile strength well above 2 GPa (Nishino et al. 1995, Page and El-Hosseiny 1983). In despite of the attractive numbers, the exploitation of putting these fibres in use as reinforcement filler has reached its bottleneck. Because of the high density of hydroxyl groups at the nanofibre surface, nanofibres are polar in nature and tend to agglomerate during drying or mixing with non-polar polymer materials. The irreversible agglomeration during drying, also known as hornification, limits the supply and usage of nanofibres to be in suspension only. This adds to the overall cost and lowers the feasibility of utilizing nanofibres. Even when suspension was incorporated into polymer matrices during compounding or extrusion, nanofibres would still form agglomerates if the surface properties of the two components do not match.

Many researches have dedicated on surface modifications to lower the polarity of nanofibres and new techniques to bypass the introduction of free nanofibres into polymer matrices, such as solution casting, impregnation and lamination. The bi-phase technique, impregnation, as well as lamination, coats or laminates films made from the nanofibre suspension to create composite. The nanofibre films were found to have a tensile strength slightly above 200 MPa and a Young’s modulus around 12 GPa, which are comparable to mild steel (Lindstrom 2007; Jonoobi et al. 2009; Abe and Yano 2009). In addition, the films have extremely low coefficient of linear thermal expansion (CLTE) at 0.1ppm/K (Nogi et al. 2009) and are optically transparent once coated with clear polymers. If a good interface can be found between nanofibre films and polymers, there lays a great potential for novel applications.

With the above facts in mind, cellulose nanofibre films can be utilized to reinforce flexible and optical polymers for the production of substrates for flexible displays, such as organic light-emitting diodes, when clarity and low CTE are both
desired. This application could not only make the dream of portable display systems come true, but also by using flexible plastic substrate, the making of display systems could shift from the conventional batch process on a glass substrate to a continuous roll-to-roll process. Okahisa et al. (2009) has well studied this particular subject by coating the nanofibre film with clear acrylic and epoxy resins and cured the nanofibre-reinforced composite by radiation curing technology. However, the tribological properties of the resulting composite, and the cure behavior were not discussed.

The proposed project is a study on the development of flexible and optically transparent nanocomposite film using nanofibres derived from wheat straw, an agricultural residue. The project consisted two sections. Firstly, the study aimed to isolate nanofibres from wheat straw using the method described in Alemdar and Sain (2008) with slightly modification. The nanofibres thus produced were characterized in their chemical composition, tensile, optical, thermal and other bulk properties. Second part of the project involved using the wheat straw nanofibre film to strengthen clear and flexible acrylate oligmers while sustaining the optical transparency and flexibility of the neat matrix using ultraviolet (UV) radiation curing. The optical and mechanical properties of the composite films were assessed, and the effect of curing time and catalyst concentration on the degree of cure was evaluated for the acrylate oligmers.
Chapter 2  Literature Background

2.1  Cellulosic Nanotechnology

Cellulose nanotechnology is the manipulation of cellulosic materials measuring 100nm or less in at least one dimension.

2.1.1  Isolation Processes of Cellulosic Nanostructures

As mentioned previously, cellulose does not occur naturally in its pure form.

Bacterial cellulose or microbial cellulose is produced by the cultivation of Acetobacter species with the presence of nutrients and sugar. Acetobacter species extrudes glucan chains into the growth medium and these chains aggregate and bundle up to form bacterial cellulose ribbons (Nakagaito et al. 2005). Bacterial cellulose has a finer structure, and is much stronger and dimensionally uniform comparing to plant cellulose. The size of the cellulose produced was reported to be 2-4nm in diameter and a few microns in length (Nakagaito et al. 2005). Raman spectroscopic technique was utilized in the study of Hsieh et al. (2008) to estimate the theoretical modulus of bacterial cellulose, which was found to be 114GPa. Bacterial cellulose is most popular as the material for medical scaffolds thanks to its excellent biocompatibility. But, the cost involved in producing bacterial cellulose is very high.

The well organized and crystallined cellulose nanowhiskers can be extracted from the mantles of tunicates, a group of underwater sea animals, or from bleached plant fibres both through acid hydrolysis. Generally, these whiskers have a high aspect ratio with length of several microns and diameter ranging from 10-20nm and a high modulus of 130-150GPa along their length (Favier et al. 1997).

In plants, cellulose is bonded with lignin, hemi-cellulose, pectin and other impurities. These impurities are amorphous in natural and usually with shorter
chains, i.e. they do not have the mechanical properties compare to pure cellulose. Therefore, these compounds have to be removed to a certain extent by chemical treatment, which is also known as delignification in the paper making process. The chemical treatment consists of two steps, pulping and bleaching. It is a proven technology and the information regarding this matter is widely available. To prepare the raw material for nanofibre production, the same scheme was applied. Studies on plant nanocellulose isolation have focused on using wood, kenaf, wheat straw, rice husks, and potato tuber as raw materials (Abe and Yano 2009; Alemdar and Sain 2008; Jonoobi et al. 2009). But, the findings are not limited to certain kinds of raw materials. The technique can be applied to a wide range of plants and agricultural residues.

Alemdar and Sain (2008) used the following chemical treatment on wheat straw. The straws were firstly swelled in 17.5% w/w NaOH for 2 h and then washed the pulp to neutral pH. The pre-treated pulp was then hydrolyzed by 1 M of HCl at 80°C for 2 hours to break down the hemicelluloses and pectin to simple sugars and hence released the cellulose fibres. The pulp was again washed with distilled water repeatedly. The pulp was treated once more with the 2% w/w of NaOH solution to remove residue lignin. Finally, the wheat straw pulp was bleached with 0.6g of NaClO₂ per gram of dry pulp equivalent. Abe and Yano (2009) used chemical treatment similar to Alemdar and Sain (2008) on rice straws using a different sequence. The dewaxed rice straw was firstly subjected to 5 times of bleaching at 70°C for 1 hour each and then treated with alkali.

Once the raw material is chemically treated, its pulp is relatively free of impurities and the fibre diameter has reduced to 30-60 microns (Hubbe et al. 2008). The pulp can be used to make plant nanowhiskers through acid hydrolysis or to produce nanofibres with further mechanical treatment. Commonly, sulfuric acid or hydrochloric acid is used in nanowhisker production, and the product is washed and dialyzed back to neutral pH (Bondeson et al. 2006). Plant nanowhiskers usually have lower aspect ratio compare to nanowhiskers from tunicates. Helbert et al. (1996) reported that nanowhiskers from wheat straw has a diameter of 5nm and a length of
150-300nm.

In order to separate the fibre bundle and individualize the nanofibres, a series of mechanical treatments have to be applied to the pulp. The mechanical treatments generally involve the usage of great shearing or impact force to break the linkage between individual nanofibres.

Alemdar and Sain (2008) firstly disintegrated the pulp into a suspension of low consistency and then passed through a refiner. Then the pulp was air dried and immersed into liquid nitrogen. The frozen pulp was crushed using a mortar and pestle or in a ball mill, then washed and passed through a fine mesh. The cryocrushed pulp was diluted into 1% consistency and mechanically defibrillated using a lab scale homogenizer at pressure higher than 300bar. The homogenizer works by pushing the fibre suspension through a minute gap which suddenly increases the flow velocity and reduces the pressure, in turn breaks down the fibre by impact and shearing forces. The majority of the nanofibres prepared in this way had a diameter of 30-40nm and the aspect ratio was around 40.

In order to improve the efficiency of the defibrillation process in terms of energy and chemical saving, several other technologies and treatments were developed. Microfluidics is an US based company which manufactures the M-110EH-30 Microfluidizer® Processor. This processor acts as a homogenizer and is designed to achieve continuous operating pressure up to 2000bar and flow rate up to 20L/hr. This technology was employed by Professor Tom Lindstrom in Sweden. A Super Masscolloider manufactured by Masuko Sanyo Co., Ltd. can also be utilized for the mechanical refining step. It is an ultrafine grinding and particularizing machine in a rotor-stator setting. The top wheel of the Super Masscolloider stays stationary while the bottom rotates. This mechanism generates large centrifugal forces that draw the pulp to shoot out from the gap between the two wheels. The fibre bundles break down and the suspension can be processed to reach a colloid state mainly due to the shearing and compression force caused by the friction between the two wheels. This machine has been widely used in Professor Hiroyuki Yano’s work in Kyoto University, Japan.
The Super Masscolloider and the Microfluidizer® promise to produce fibres with uniform sizes and clean-up is relatively simple. Also, because these two machines use large force and high pressure, and the sample can be fed continuously, the energy and time applied in defibrillation process can be reduced, and large quantity of nanofibres can be readily produced. A pilot nanofibre production line has established in early 2010 at the Centre for Biocomposites and Biomaterials Processing, University of Toronto. It is equipped with a high shear defibrillator, a bench scale high pressure homogenizer and other necessary resources involved in producing nanofibre from scratch.

Several studies have investigated the potential of using chemical or enzymatic aids in simplifying the defibrillation process. A solution of lithium chloride in N,N-dimethylacetamide has proven to swell the cellulose pulp and make it more susceptible to separation into nanofibres (Oksman et al. 2006). An enzyme derived from the infected Dutch elm tree was used to treat the bleached pulp. The enzyme targets the amorphous regions of cellulose making it easy to separate into smaller sizes. Nanofibres produced using this treatment in combination with refining, cryocrushing and homogenization have proven to have higher aspect ratio (Janardhanan and Sain 2006). Paakko et al. (2007) also investigated the potential of using an enzyme, endoglucanase, in improving the efficiency of defibrillation process.

Chemical composition of the bleached pulp can also influence the defibrillation process. Iwamoto et al. (2008) mentioned that hemicellulose in the pulp served as inhibitors of the coalescence of nanofibres, therefore, contributing to the ease of nanofibrillation.

### 2.1.2 Surface Modification

Surface modification is necessary to overcome the challenges imposed by the hydroxyl groups at the nanofibre surface when comes to drying and composite making.
Chemical modifications reduce the polarity and thus improve the cellulose compatibility and dispersion in the matrix. On the other hand, chemical modification can decrease the crystallinity of nanofibres leading to a possible reduction of their reinforcing potential (Sassi and Chanzy 1995). There are several chemical treatments developed which add new functional groups to the cellulose chain. Coupling agents are one of the most widely used chemical substances for improving adhesion. They form a bridge of chemical bonds between the nanostructures and matrix, with one end of these coupling agents attached to the OH group of cellulose and the other end reacts with the functional groups of the matrix. Examples of coupling agents are silane, maleic anhydride (MA), maleic anhydride-polypropylene copolymer (MAPP). Grafting is another way to effectively add functional group to the nanostructures. Grafting efficiency, percentage and frequency determine how compatible the nanostructures are with the matrix (Thomas et al. 2001). Various methods were reported to modify the surface of nanofibres, such as TEMPO oxidation, acetylation and partial carboxymethylation (Saito et al. 2006; Sassi and Chanzy 1995; Eyholzer et al. 2010). Eyholzer et al. (2010) could successfully produced water-redispersible nanofibre powder by partial carboxymethylation. The onset degradation temperature of modified nanofibres, however, decreased from 300 to 200°C due to the reduction in crystallinity. This would limit their usage only to the polymers that do not require processing temperatures above 200°C.

Physical modifications do not change the chemical composition of the nanostructure or the matrix. Rather, they modify the structural and surface properties, thereby influencing the mechanical bonding with each component. Electric discharge, like corona and plasma, has been used commonly in treating the surface of natural fibre. Plasma treatment mainly causes chemical implantation, polymerization, free radical formation, that can change the surface roughness and lead to increase in adhesion (Akovali and Dilsiz 1996). Corona treatment is an effective way to change the surface energy through surface activation. The oxygen molecules exposed under the corona discharge break down into their atomic form and can bond to the surface of cellulose and matrix. This results a chemically
activated surface for grafting matrix to the nanostructures (Gandini and Belgacem 2005).

A way to evaluate the effectiveness of the surface modification and analyze the composite interface is to assess each constituent in advance, such as contact angle measurement, inverse gas chromatography. Another way is to measure the mechanical properties of composites via various tensile, compression and shear tests to check whether there are any property improvements, or imaging the fracture surfaces to see if there is fibre pullouts as opposed to breakage.

2.1.3 Composite Assembly

Uniform mixing and sufficient wetting of the nanostructures are the two important factors determining the properties of final nanocomposites as poor dispersion will create weak points in the composites and affect their final mechanical performance. Also, swelling of cellulose nanostructures due to moisture and damage caused by high processing temperature and force should also be avoided during processing. Nanostructure loading percentage needs to be carefully decided through experiments in order to avoid over loading and possibilities of adverse effects according to percolating theory (Chakraborty et al. 2006, Hubbe et al. 2008). Generally, loading of nanofibres can be higher than their larger entities because of their miniature size.

With the above considerations in mind, cellulose nanocomposites can be prepared either by liquid phase processing with water/solvent soluble matrices or solid phase processing with water immiscible matrices. Liquid phase processing is also known as film casting where nanostructures are well mixed with selected matrix material in water or solvent and the mixture is evaporated under vacuum or with the help of a freeze dryer. In solid phase processing, as its name implies, the filler and matrix are at their dry state when mixed. The common technology used is impregnation, while compounding followed by either extrusion or injection molding achieved little success. In the study conducted by Iwatake et al. (2008), 10%
nanofibre slurry and polylactic acid (PLA) were mixed in excess acetone and then solution casted. The thus formed composite was compounded and tested for tensile properties. The tensile strength and Young’s modulus went up by 17 and 25% respectively. In contrast, the direct mixing of nanofibre slurry to melted PLA during compounding lowered the tensile strength by 10%.

Electrospinning has allowed nanostructures to be combined with desired matrices and be spun into nano-scaled composite fibres. Surfactants and magnetic treatment can be used in both liquid and solid phase processing to improve nanostructure dispersion and orientation (Bondeson and Oksman 2007; Kvien and Oksman 2007; Hubbe et al. 2008).

All-cellulose composites have recently been introduced. They are the self-reinforced composite which contain only cellulose itself. They are prepared either by impregnating cellulose matrix into cellulose fibres or by selective dissolving the skins of cellulose fibres to form a matrix-like phase that bonds adjacent fibres together. The selective dissolution method can create a well-defined fibre/fibre interface that has minimum voids and stress concentration since a gradual change in properties takes place rather than the sudden change between the components in conventional composites (Eichhorn et al. 2010). In the study conducted by Nishino et al. (2004), ramie pulp was firstly dissolved in N,N-dimethyl acetamide containing 8% of lithium chloride. Then manually woven ramie fibres were impregnated under a reduced pressure for 12 hours. The gel-like matrix was then dried and tested. Impressive tensile strength and Young’s modulus was achieved at 480MPa and 20GPa respectively. 410MPa in tensile strength and 18GPa in Yong’s modulus was also reported for all-cellulose composite prepared with bacterial cellulose in the same way.

2.1.4 Applications

The advancements in isolation process, surface modification and composite assembly have allowed the nanostructures with their advantages to be used in a wide
range of high-tech applications, such as medical scaffolds and drug delivery carriers, durable light-weight building materials, food and rheology additives, packaging materials and optically transparent films (substrates for portable display systems) (Hubbe et al. 2008; Ioelovich 2008).

Bacterial nanocellulose is currently the most studied for its applications in scaffolds, artificial blood vessels and cosmetic tissues. Electrospinning technology has helped to develop nanofibrous scaffolds with extremely high surface-to-volume ratio, tunable porosity, and excellent malleability for medical uses (Liang et al. 2007). Juntaro et al. (2008) grafted bacterial cellulose onto micrometer scaled sisal fibres. The grafting created many “arms” on the surface of sisal fibres and enhanced their interaction with the polymer matrix, poly(l-lactic acid) (PLLA). The improved adhesion resulted in almost 80 and 400% increase in tensile strength and Young’s modulus respectively.

Cellulose nanostructures have proven to be optically transparent as larger diameter fibrils have been excluded and distribution has been improved. When combined with optical polymers like acrylic and epoxy resins with impregnation or lamination process, the resulting composites can transmit up to 80% of visible light and can reduce the coefficient of thermal expansion by 10 folds comparing to the pure polymer (Yano et al. 2005). This type of cellulosic nanocomposites is excellent materials for making substrates of display systems. The composites can be either flexible or rigid depending on the selection of matrices, and would be suitable for portable display systems or glass replacement.

The dispersion of cellulose nanostructures has unique rheological feature (Ioelovich 2008). Nanostructures have large attraction to surrounding water molecules through exposed hydrogen bonding and form a highly viscous gel-like system in water. Due to this feature, nanostructures are very popular additives for food, paint, cosmetics and medicines to avoid phase separation and improve texture.

The miniature size of cellulose nanostructures has the advantage over their large entities for reinforcing the cell wall of polymer foams which are typically only a few microns thick. Svagan et al. (2007) prepared biofoams in liquid phase based on
potato starch and cellulose nanofibres from wood pulp. The water in the mixture was removed by freeze drying. The energy absorption during compression was doubled with 40% of nanofibre loading compared to the neat starch foam. The findings can be applied to packaging or insulation material developments.

Adding cellulose nanostructures to paper composition can increase the strength of paper by increasing the direct inter-fibre contact (Ioelovich 2008). Cellulosic nanostructures perform outstandingly as an oxygen barrier in the polymer matrices. This feature makes the nanocomposites an excellent candidate for food and pharmaceutical packaging. Nanowhiskers can help to make uniform nanopore materials when combined with desired and heat-resistant end materials. The whiskers are well dispersed in the matrix and then the composite is incinerated leaving nano-sized pores in the material (Dujardin et al. 2003). Cellulose nanostructures are not conductive on their own. However, research has shown that when conductive polymers, for example, PEDOT-PSS, are deposited onto cellulose, a conductivity of 10 S/cm can be achieved. The conductive nanocomposites can be used as sensors and transistors (Agarwal et al. 2006).

2.1.5 Summary

Cellulosic nanostructures have unique mechanical, optical, electrical and chemical properties that can be utilized in a variety of diverse applications. Successful and positive results have been achieved through the efforts of many dedicated researchers and studies on the isolation, surface improvement and assembly of nanocomposites. However, the long-term durability of cellulose nanocomposites may become a major concern since there is no long-term data that compares the lifetime of these composites with conventional made alternatives. Commercialization of nanocomposites also remains as a question to be resolved. The high initial capital investment, the lack of information on the scaling-up process, and the lack of facilities to produce large quantity of cellulose nanostructure samples have prevented many viable ideas to emerge from lab to market. Resolving the above
concerns would be the next step to drive the cellulose nanotechnology forward.

2.2 Radiation Curing

Radiation curing is defined as the conversion of reactive liquid to solid through chemical reactions induced by radiation energy (Rechel 1995). Curing initiated by radiation in the infrared, microwave and radio frequency range is called thermal curing, whereas curing initiated by ultraviolet (UV) and electron beam (EB) irradiation through electronic excitation and ionization is usually known as UV/EB curing. The latter subject and its subtopic, free radical curing, are the focuses of this review.

Radiation technology did not emerge until the concerns for conventional water and solvent based industrial coating and adhesives have become apparent. The conventional formulated coatings and adhesives are low in solids which consume excessive energy in evaporating the diluter; and the use of volatile solvent aroused the concern for the environment. On the other hand, UV/EB along with thermal curable systems are energy efficient and free of solvents. Berejka (1999) quoted that the energy consumption of UV/EB curable, water based and solvent based system was 7cal/g, 810cal/g and 177cal/g respectively. In additional, UV/EB curing process requires relatively low capital investment and operating cost, the material can be cured rapidly resulting in high productivity and little or no heat buildup during the curing process which opens the door for heat sensitive substrates. Above are the characteristics of UV/EB curable system which have attracted much attention and its application has expanded from coatings and adhesives to lithography, dental casts and so on (Rechel 1995).

2.2.1 Source of Radiation

The source of electromagnetic radiation usually comes from ultraviolet and electron beam. Other sources like lasers and visible radiation are less common. UV and EB curable systems are essentially different as UV generates photons and EB generates electrons (Rechel 1995).
Photons generated by UV source have energies between 2.2 and 7.0eV (Drobny 2003). They tend to be absorbed mainly at the surface of the material. In additional, they do not have the sufficient energy to break chemical bond and produce electronic excited ions leading to solidification of the starting material (Koleske 2002). Photoinitiators which act like catalysts are utilized to generate reactive species that will initiate the curing process. This is one of the biggest distinctions between UV and EB curing.

If electron beam is applied as the radiation source, the use of photoinitiators can be avoided. This is because EB generates electrons with energies between 100 to 300kV (Drobny 2003). They are small enough and contain high energy to penetrate matters and form ions, radicals and excited molecules within the starting material along the way. Photons from UV radiation with sufficient energy can produce electrons, but it is not usually available (Koleske 2002).

Generally, the energy required for photoinitiators or starting monomers to transform from their ground to excited state is 2 to 8 eV. The excited molecules are then able to undergo chemical reaction with the monomers in the system to form propagating species, which then initiates solidification of reactive liquid. Ionization of starting monomers, which happens in EB curing, requires more energy upon the excitation. Ionization process generates positive ions and secondary electrons. The positive ions have the same function as the photoinitiator. They are transformed into free radicals in compounds that contain ethylenic unsaturation (linear carbon-carbon double bond), or Lewis and Bronsted acid in cyclic compounds. The secondary electrons lose their excess energy, become thermalized and add on to the monomers (Mehnert et al. 1997; Drobny 2003).

UV radiation has wavelength from 40 to 400nm in the electromagnetic spectrum. However Vacuum UV in the range of 40 to 200nm is not suitable for UV curing. UV energy can be generated from electricity in either electric current or microwave energy form in a bulb filled with mercury. Both methods create plasma which generates UV energy (Drobny 2003). When choosing UV lamps, the wavelength of irradiation should be carefully decided. In colored or opaque materials, the
wavelength should be at the point where the spectrums of photoinitiator and photoinitiator with starting material give the biggest difference. For clear materials, the wavelength only needs to match the absorption peaks of the photoinitiator (Crivello et al. 1998). With these rules in mind, the radiation energy will be converged in the excitation of photoinitiator rather than absorbed by the starting monomers. UV curing equipment essentially consists of three parts, bulb, housing with reflector and power supply. The UV irradiance, or intensity, is usually expressed as the radiant power per unit of surface area, W/cm².

In EB curing, electrons are generated in a high vacuum by a heated cathode. The electrons are then accelerated in an electrostatic field between the cathode and anode. The latter requires a particle accelerator. An EB generator is much more complex than UV.

Overall, EB curing consumes less energy and has higher efficiency and productivity. The operating cost is also lowered because no photoinitiators are required. However, the initial investment in capital is much higher compared to UV curing (Koleske 2002).

### 2.2.2 Types of Photoinitiators

Photoinitiators are organic molecules that become electronically excited after energy absorption. When at their excited state, photoinitiators photolyze or degrade directly or indirectly into free radicals or cations (Koleske 2002).

#### 2.2.2.1 Free Radical Photoinitiators

Free radical photoinitiators are generally divided into two types, Norrish Type I and Norrish Type II.

Type I photoinitiators are compounds that undergo a homolytic cleavage reaction and generate two radicals when exposed to radiation (Drobny 2003). Homolytic fragmentations that take place between a carbonyl group and an adjacent carbon are classified as α-cleavage. Homolytic fragmentations that take place at a
bond in the β-position (not directly adjacent to a carbonyl group), or at weak bonds like C-S, C-Cl and O-O, are classified as β-cleavage (Fouassier 1995). Common Type I photoinitiators are benzoin ether derivatives, benzilketals, α-hydroxyl alkylphenones, α-aminoketones and acylphosphine oxides (Crivello et al. 1998; Drobny 2003).

Type II photoinitiators can not spontaneously fragment and generate free radicals like Type I photoinitiators. These photoinitiators need the presence of a synergist that will interact with the excited molecules and form free radicals by electron transfer and hydrogen abstraction mechanism (Koleske 2002). Synergists are usually tertiary amines which contain a nitrogen atom next to an alpha carbon. The Type II photoinitiators are typically aromatic ketones (Drobny 2003).

2.2.2.2 Cationic Photoinitiators

Cationic photoinitiators are onium compounds that photolyze to form Lewis or Bronsted acid when excited under the influence of UV radiation. The acid in turn catalyzes the desired polymerization process (Fouassier 1995).

2.2.3 Mechanism of Photoinitiated Curing

2.2.3.1 Free Radical Curing

Photoinitiated free radical curing proceeds through three main steps: initiation, chain propagation and termination (Fouassier 1995; Koleske 2002; Drobny 2003).

The photoinitiators absorb radiation energy and photolyze into two free radicals. These free radicals are then combined with monomer or oligomer M to form initiated species.

\[
\text{Initiator} \xrightarrow{\text{energy}} R_1 \, \bullet + R_2 \, \bullet \\
R_1 \, \bullet \text{ or } R_2 \, \bullet + M \rightarrow R M_1 \, \bullet
\]

In the propagation step, the initiated species and additional monomers or oligomers are consumed to from propagating species.

\[
R M_1 \, \bullet + M \rightarrow R M_2 \, \bullet
\]
Finally, the chain propagation is terminated when a free radical meets an initiated or propagating species, or when two initiated or propagating species meet.

\[ R \cdot + RM \cdot \rightarrow R - RM \]
\[ RM_1 \cdot + RM_2 \cdot \rightarrow RM_1 - RM_2 \]

The presence of oxygen decreases the efficiency of photoinitiated free radical curing by scavenging the free radicals, and initiating and propagating species (Drobny 2003). Oxygen can quench an excited photoinitiator back to its ground state before it splits into free radicals. The oxygen then gains the energy returned by the photoinitiator and from singlet oxygen, which can retard the polymerization by forming peroxides and hydroperoxides with the monomers or oligomers in the system. Oxygen inhibition leads to incomplete cure of the system resulting in molar weight reduction and tacky surface. Even small concentration of oxygen, \(10^{-3}\) molar, was reported to deter the curing process. To prevent this undesired phenomenon, the curing process can be carried out under a nitrogen blanket or by covering the material with shielding films, for example, polyester sheet. Gruber (1977) also suggested that using Norrish Type I and II photoinitiators can reduce oxygen inhibition. This is because of the peroxides generated from oxygen depletion can abstract hydrogen from monomers and oligomer which aid the mechanism of Type II photoinitiators. Other methods include addition of oxygen scavengers and surface-active initiators, increase photoinitiator concentration, and increase UV intensity (Koleske 2002).

2.2.3.2 Cationic Curing

Cationic photoinitiation is generally based on a ring opening of the oxirane group. Photoinitiated cationic curing proceeds through three main steps: initiation, propagation and termination. Cationic photoinitiator interacts with an active hydrogen source under the UV radiation to form a protonic acid which then undergoes propagation by reacting with epoxides to from initiated epoxide. The initiated epoxide then reacts with other epoxide molecules to form the polymerized
product. The termination only takes place when the monomer is exhausted or the system is neutralized by the presence of basic compounds (Crivello et al. 1998; Koleske 2002; Drobny 2003).

2.2.4 Types of Starting Materials

Free radicals can initiate the curing of a variety of compounds that contain carbon-carbon double unsaturation. Acrylate and methacrylate systems are the most widely used materials in UV curable and free radical initiated curing processes. They are available in mono- and multifunctional monomers, and acrylate oligomers, such as epoxy acrylate, urethane acrylate. The general formula of an acrylate is \(H_2C=CH-COOR\). Acrylate with \(CH_3\) group instead of a hydrogen atom on the second carbon is a methacrylate (Koleske 2002). Methacrylates are less reactive than acrylates, but are less toxic and cause less skin irritation. Other free radical curable systems are unsaturated polyesters, unsaturated esters and thiol-ene (thiols and olefins) systems (Drobny 2003).

Cations initiated curing is dedicated to cyclic compounds, like epoxides, and certain unsaturated compounds, such as vinyl ethers. Although vinyl ethers can also be cured by free radical curing, their response to UV radiation is far less sensitive compared to acrylates or methacrylates. Therefore, vinyl ethers usually undergo cationic curing (Koleske 2002).

The photoinitiated curing process involves polymerization and sometimes polymerization and cross-linking simultaneously depending on the functionality of the starting material. Monomers or oligomers with functionality less than two undergo linear polymerization where only chain addition occurs. Multifunctional monomers and oligomers, on the other hand, yield three dimensional cross-linked networks. The cross-linked curing can result in products with better solvent resistance, harness and heat resistance (Drobny 2003; Fouassier 1995).

Monofunctional monomers are usually used to dilute the formulation to the suitable viscosity. Acrylate oligomers usually have di- or multifunctionality (Fouassier
Among all acrylate oligomers, urethane acrylates, including urethane methacrylates, are the highest performance oligomers offered in the radiation cure industry. They offer chemical and heat resistance, and good adhesions. The end product is tough, with good abrasion resistance yet flexible (Drobny 2003). Urethane acrylates are synthesized by the reaction of isocyanate with a polyester or polyether polyl which form a urethane unit terminated by isocyanate. The urethane unit is then reacted with hydroxyl-functional acrylate monomers. Acrylation provides the ethylenic unsaturation to the end of the oligomer (Webster 1997). Therefore, urethane acrylate oligomer structures can generally be illustrated as follows:

acrlyate/methacrylate – oligomer backbone – acrylate/methacrylate

The functionality of the isocyanate component determines the functionality of the urethane acrylates. Lower functionality results in lower reactivity, better flexibility and lower viscosity. The aliphatic or aromatic nature of urethane acrylates is also determined by the structure of the isocyanate. Aromatic urethane acrylates are generally cheaper but less flexible compare to aliphatic urethane acrylate. The choice of polyl used during the synthesis is either esters or ethers. The options of isocyanates and polyols allow considerable latitude in the development of urethane acrylates (www.sartomer.com).

Other acrylate oligomers are produced in the similar way as urethane acrylates but with different oligomer backbones.

2.3 Engineered Films for Display Technologies

Display technology is a dynamic and continuously evolving subject. Since the invention of cathode ray tube more than 100 years ago, the display systems have advanced rapidly as technology improves in manufacturing process, materials, conducting layers. Nowadays, customers have many options in choosing display systems that are slender, light-weighted and have excellent color profiles. But human imagination would never stall but move forward for the better. The next anticipated trend in display systems would be a paper-thin flexible flat panel display. Defined by
Slikkerveer (2003), a flexible flat panel display is constructed of thin and flexible substrates that can be bent, flexed, conformed, or rolled to a radius of curvature of few centimeters without losing its functionality.

A flexible substrate is the essential component of a flexible flat panel display. Thin glasses, metal foils, and polymers are among the choices of material for the substrate (MacDonald 2004). Flexible flat panel display based on fabric was also reported (Shiyanovskaya et al. 2006).

Despite its excellent resistance to heat and chemicals, barrier properties and compatibility with other components within a display system, conventional glass substrate is rigid and can only be made in a batch process (Crawford 2005). Glass becomes flexible when the thickness is below 200 microns (Plichta et al. 2003). The production and feasibility of thin glass, however, is limited by the current technology to create substrate that has desired thickness and surface quality. Therefore, many developments are on going (Plichta et al. 2005).

Metal foils can endure the high processing temperature of subsequent display layers and provide a good barrier against water and oxygen. Nevertheless, it is not suitable for transmissive displays and can not handle multiple bends (Choi et al. 2008).

On the other hand, polymeric material is flexible and with proper add-ons to the manufacturing process, the making of finished product can go roll to roll. To replace glass, a polymeric material must meet the criteria listed in Table 1 below (MacDonald 2004, Choi et al. 2008). As of now, no plastic film offers all the properties listed. Therefore, multilayer-engineered plastic substrates will be required (MacDonald 2004).

Several polymers are considered potential candidates for flexible substrate as they meet most of the criteria. They are semi-crystallined polyethylene naphthalate (PEN), polyethylene terephthalate (PET) and polyetheretherketone (PEEK), amorphous polycarbonate (PC), polyethersulphone (PES), and amorphous polyarylates (PAR), polycyclic olefin (PCO) and polyimide (PI), which have high glass transitional temperature and can not be melt processed (Choi et al. 2008).
Good surface quality, and low water and gas permeability were achieved by coating PES with barrier layers and a protective layer at the surface (Ito et al. 2005). By incorporating nanofibre films into flexible polymers through impregnation or lamination process, the thermal stability of the substrate could be significantly improved without much sacrifice in transparency (Nakagaito et al. 2010).

**Table 1** Minimum property requirements for polymer based flexible display substrates. (Source: MacDonald 2004, Choi et al. 2008)

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Optical</strong></td>
<td></td>
</tr>
<tr>
<td><em>Total light transmittance over visible wavelength range</em></td>
<td>&gt;85%</td>
</tr>
<tr>
<td><em>Haze</em></td>
<td>&lt;0.7%</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
</tr>
<tr>
<td><em>Degradation temperature</em></td>
<td>&gt;150°C</td>
</tr>
<tr>
<td><em>Coefficient of linear thermal expansion (CLTE)</em></td>
<td>&lt;20ppm/°C</td>
</tr>
<tr>
<td><strong>Barrier properties</strong></td>
<td></td>
</tr>
<tr>
<td><em>Water vapor transmission rate per day</em></td>
<td>1-10g/m², &lt;10⁻⁵g/m² for OLED</td>
</tr>
<tr>
<td><em>Oxygen transmission rate per day</em></td>
<td>1-10ml/m², &lt;10⁻⁵ml/m² for OLED</td>
</tr>
<tr>
<td><strong>Average surface roughness</strong></td>
<td>&lt;5nm</td>
</tr>
<tr>
<td><strong>Chemical resistance</strong></td>
<td>Able to resist acid, base and solvent</td>
</tr>
<tr>
<td><strong>Flexibility</strong></td>
<td>Able to bend over 1 inch diameter radius 1000 times</td>
</tr>
</tbody>
</table>
Chapter 3  Materials and Methodology

3.1  Materials

Materials involved in the course of this study were wheat straw supplied by the University of Guelph, acrylate resins from Sartomer and photoinitiators from Ciba Specialty Chemicals.

3.1.1  Wheat Straw

Chopped and dried wheat straw was a generous gift from the University of Guelph. The wheat straw was collected from the farms in Guelph region, Ontario.

3.1.2  Acrylate Resins

The acrylate resins used in the study were kindly supplied by Sartomer. Three acrylate oligomers were studied and they were denoted as Resin 1, 2 and 3. Resin 1 is a low viscosity acrylic oligomer. It was chosen due to its high refractive index and low viscosity. Resin 2 and 3 are aliphatic urethane acrylates produced with polyester polyols. They were chosen because urethane arylates produce tough, flexible materials that exhibit good abrasion resistance. Resin 3 in particular was reported to have good abrasion resistance. However, Resin 2 and 3 are high in molecular weight and viscosity that made them less desirable in terms of handling. A difunctional acrylate monomer was suggested by Sartomer as a diluent for viscous oligomers. It is widely used when flexibility and adhesion are demanded in the end product. By mixing Resin 2 or 3 with this diluent at 40% did not lower the viscosity to the desired level even at elevated temperature. Therefore, it was not investigated further. The molecular structures of these resins are proprietary, so are their other properties. Rather the ranking of molecular weight was provided as Resin 1 has the lowest molecular weight followed by Resin 2 and Resin 3.
Table 2 below summarized some of the properties of these acrylate oligomers determined by the author. The viscosity and density were retrieved from the certificate of product compliance forms. Glass transitional temperature, T_g, was measured again by using a differential scanning calorimeter (DSC) for resins cured 2 minutes on each side with 1% of PI1 and 0.1% of PI2 under 18.85mW/cm² of UV intensity. The sample thickness was controlled at 0.5mm. The same curing condition was used for determining the refractive index through dielectric constant measurement and tensile properties. For detailed descriptions on resin curing, DSC analysis, refractive index measurement and tensile test please refer to the latter sections (3.2.3).

Table 2 Physical properties of acrylate oligomers from Sartomer.

<table>
<thead>
<tr>
<th>Property</th>
<th>Resin 1</th>
<th>Resin 2</th>
<th>Resin 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Name</td>
<td>Acrylic Oligomer</td>
<td>Aliphatic Urethane Oligomer</td>
<td>Aliphatic Urethane Oligomer</td>
</tr>
<tr>
<td>Functionality</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Viscosity (cps)</td>
<td>350@25°C</td>
<td>2750@60°C</td>
<td>5850@60°C</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.16</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>T_g (°C)</td>
<td>28</td>
<td>9.7</td>
<td>54</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.32</td>
<td>1.26</td>
<td>1.20</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>21.2</td>
<td>13.8</td>
<td>24.7</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>0.34</td>
<td>0.06</td>
<td>0.59</td>
</tr>
<tr>
<td>Elongation at Yield (%)</td>
<td>44</td>
<td>28</td>
<td>20</td>
</tr>
</tbody>
</table>

3.1.3 Photoinitiators

Samples of two types of photoinitiators suitable for acrylate resins were supplied by Ciba Specialty Chemicals. One of them belongs to the α-hydroxyketone chemical class, while the other belongs to the bis acryl phosphine chemical class. They are denoted as PI1 and PI2 in the rest of the study.

Photoinitiators in the (bis) acryl phosphine family are widely used in the curing industry because of its high radical yield and ability to cure thick film. They also undergo photobleaching process after UV exposure which gives colorless appearance of the cured resin. However, strong oxygen inhibition is observed in the curing that involves this type of photoinitiators. Ciba suggested using PI1 to ensure surface cure.
This α-hydroxyketone photoinitiator is also a non-yellowing one. Therefore, the combined formula should give colorless end product.

PI2 is a Norrish Type I photoinitiator, which undergoes α-cleavage to form free radicals (Szablan et al. 2007). On the other side, PI1 can form free radicals either through Type I α-cleavage or Type II hydrogen abstraction (Visconti and Cattaneo 2000). This fact explained the reason why the manufacturer suggested to use the two photoinitiators together as Type II photoinitiators can reduce oxygen inhabitation when combined with Type I photoinitiators (Gruber 1977).

3.2 Methodology

3.2.1 Material Preparation

3.2.1.1 Production of Nanofibres

The nanofibre production from wheat straw consisted of three parts, pretreatment, chemical treatment to remove lignin, hemicellulose and other impurities, and mechanical treatment to defibrillate. The chemical process was based on the work published by Alemdar and Sain (2008) with minor alternations. The yield of bleached wheat straw pulp was found to be 35%.

After the chemical treatment, the bleached pulp with 2% consistency was fed to a high shear defibrillator. Four sets of nanofibre suspensions were produced. All sets went were subjected to same chemical treatment. Set A was a test run to check the optimal number of passes to yield quality nanofibres in the defibrillator. The bleached pulp went through 50 passes and for every 10 passes a sample was collected for analysis. Set B, which was used for composite making, was run at the same condition for 20 passes only. Half of the amount was saved after 10 passes. For Set C, the bleached pulp that went through 10 passes in the defibrillator from Set B was fed into a high pressure homogenizer for 10 passes. Set D was mechanically defibrillated by the high pressure homogenizer only for 50 passes. The suspensions of Set A and B and the nanofibre films made from these suspensions were denoted as
“Set ranking”-“Number of Passes”. For example, a sample went through the defibrillator for 10 passes from Set A was referred as A-10. Samples from Set C and D were denoted as is.

**Figure 1** Flow chart of different sets (A to D) of nanofibre suspension prepared.

3.2.1.2 Formation of Nanofibre Film

In this section, the method to prepare dried nanofibre films was discussed. Mechanically defibrillated fibre suspension was firstly measured for its consistency. The consistency varied from 0.5 to 1.3% for different batches. A certain amount of suspension containing 0.3 g of dry fibre was drawn and diluted to 0.2% consistency. The diluted suspension was then mixed with a magnetic stirrer for over night in order to re-disperse the fibres to reach homogeneous state.

After the mixing was finished, the 0.2% suspension was vacuum filtered to form nanofibre film. The filtration was done in a 90mm diameter Buchner funnel equipped with a piece of Supor® membrane disc filter from Pall Life Sciences. The pore size of this membrane was 0.1μm, which was small enough to retain the nanofibre network but filter out water. Supor® membrane was made from hydrophilic polyethersulfone which repels the hydrophobic cellulose, making it easier for the film to be peeled off than the conventional paper filters.

The filtration process was prolonged on purpose by placing the shiny side of the filter membrane up and keeping the vacuum force at minimum. This was to achieve better fibre settlement. This was also the reason why the fibre suspension was diluted to 0.2%. Working with diluted samples helped to achieve films with even thickness and smooth surface, but the dilution was mainly aimed for better fibre
settlement. Lindstrom (2007) stated that if the fibres lay down in a one-plane fashion, the mechanical properties would be improved because those out-of-plane fibres create weak spots in the network.

Once most of the water has been filtered out, the contents in the funnel was carefully taken out with the aid of a spatula. The nanofibre film was then peeled off from the filter membrane. At this moment, the film still contains around 80% of water. But it was easier to separate the film from the membrane now than wait till the film was completely dried. Also, when the film was still relatively wet, it would experience less surface breakage and marking during the peel-off.

The fibre film was then sandwiched between two 350 mesh nylon cloths and packed with more paper filters on each side. The paper filters were used to absorb water from the film. The stack was then placed under a 50psi press for 30 minutes and stand to dry at room temperature with a load on top for 48 hours. Without removing the load, the films were further dried at 85°C for 12 hours. The fibre films were then kept in a desiccator to prevent moisture absorption.

The dried fibre films had a density ranging from 1.20 to 1.55g/cm³ depending on the weight of the load put on top of the samples while they were drying. The density of the film had an impact on the mechanical and optical properties of the film. At the end, a 10kg weight was decided to apply on top of the drying films. Please refer to the sections of 4.1.5 and 4.1.6 for details.

3.2.1.3 Preparation of Nanocomposite Film

A bench scaled UV curing equipment was a gift from Professor Winnik's group in Chemistry Department. It had a parabolic reflector allowing even distribution of irradiation over the housing area. The housing area was approximately 15 by 15 centimeter square. The device could hold two compact bulbs in bi-pin setting. According to the absorption peaks of the photoinitiators, two 9W fluorescent UVA bulbs (PL-S 9W/10/2P UNP) were purchased from Philips Lighting. The bulbs irradiate UVA broadband from 330 to 400 nm peaking at 367nm. When lighted, the intensity
created by both bulbs at 360nm wavelength was measured to be 18.85mW/cm² using a VLX 3W radiometer manufactured by Vilber Lourmat.

The lighting system in the laboratory may emit radiation at the wavelength that would be useful to start the curing process. This situation was undesired because it would cause local polymerization in the not so well mixed mixture of resin and photoinitiator, and the polymerization in advance would make the resin more difficult to work with as it will increase the viscosity. Therefore, the following steps were conducted with limited light source.

Certain amount of acrylate was drawn from the bottle to a glass beaker and weighted. 1% of PI1 and 0.1% of PI2 were added. The mixture was then sonicated in for 2 hours or until the photoinitiator was fully dispersed. Acrylate resins with higher viscosity usually take longer time. The use of a sonicator was to minimize the bubble formation caused by mechanical stirring. This was again crucial for viscous resins. The sonication process also generated heat which helps to reduce the viscosity of resins making them easier to spread. The temperature was well controlled to not exceed the suggested temperature listed on the MSDSs of the resins, usually 60°C.

The prepared fibre film was first dried at 85°C for at least 2 hours prior to the making of composite to eliminate moisture that would repel the acrylate resins at the fibre surface, thus, reduce the transparency as the resins are not water soluble. The dried film was then dipped into the mixture of resin and photoinitiators, and together placed in a vacuum oven at a pressure of minus 28 inches of mercury for 1 day before curing to provide sufficient wetting.

Next, the doped fibre film was taken out and laid down on a piece of Mylar® sheet (DuPont Teijin Films), and sandwiched in between with another piece of Mylar® sheet. The Mylar® sheet not only acted as an oxygen barrier, but also helped to spread out the resin and make the surface smooth. According to its absorption spectrum, Mylar® sheet does not interfere with the curing process. In other words, the absorption peak of Mylar® sheet is not in line with the photoinitiators. Therefore, it would not take in the energy which is necessary to excite the photoinitiators to form free radicals.
A rectangular metal block was used as a scraping tool to push out any bubbles and control the thickness and fibre loading of the final composite. Sometimes, a heating block was used to help the spreading of viscose resins.

Once ready, the sandwiched system was placed under the UV device and cured for 2 minutes on each side.

3.2.2 Characterization of Nanofibre Suspension and Films

3.2.2.1 Nanofibre Morphology

The physical structure and morphology of treated wheat straw fibre from Set A to Set D were studied by transmission electron microscope (TEM/HD-7000, Hitachi). A drop of diluted fibre suspension was pipetted onto a carbon-coated 400-mesh copper grid. The drop was allowed to settle for 1 minute and the excess water was absorbed off by a tissue paper. The microscope was operated at 75KW with 50mA current.

3.2.2.2 Chemical Composition

Chemical composition of the original, alkaline treated and bleached wheat straw were analyzed for their solvent soluble extractive, alpha-cellulose, hemicelluloses and lignin contents. The chemical characteristics of the wheat straw after different stages of chemical treatment implied the efficiencies of these treatments. The alkaline treatment was mainly targeted to remove the hemicellulose while the bleaching served to remove the lignin in wheat straw. The chemical compositions were assumed to stay constant during the mechanical treatment.

Raw wheat straw and chemically treated pulps were firstly dried at room temperature then grinded in a Wiley mill to 40 mesh size prior to any tests. The moisture content of these samples was measured separately in order to correct the chemical compositions of samples to oven-dry weight basis. A minimum of two replications were carried out on all samples and for all tests.
Extractives

Extraction was done only on the raw and alkaline treated wheat straw as the extractives in bleached wheat straw was negligible after 2 steps of chemical treatment. The test procedure was based on TAPPI T 204 om-88 and ASTM D1105-96.

Three 0.3-0.5g of samples were accurately weighted and wrapped in a piece of kimwipe then secured with strings. The moisture content of kimwipes and strings were measured for correction. Extractive free sample was also prepared for future lignin and holocellulose determinations by placing a larger quantity of sample (5g) inside two timbles.

The bags were placed in one soxhlet and the two timbles each occupied one soxhlet setup. The samples were first extracted by a highly non-polar solution consisting 2 parts of toluene and 1 part of ethanol until the solvent in the siphon ran colorless, usually 4-6 hours. A second round of extraction using only ethanol was conducted to solubilise and wash out any compounds left from the first extraction stage. This step took around 4 hours to complete. For the final extraction, highly polar distilled water was used. The bags and the timbles were submerge in 1L boiling water for one hour. The bags used for extractive determination were oven-dried at 105°C for 24 hours before weighing.

The quantity of extractives of the sample was determined by the oven-dry weight of the bag minus the weight of kimwipes and strings then divided by the original sample weight corrected with moisture content. The samples which would be used for future tests were removed from the timbles and left to dry at room temperature. The moisture content was later measured.

Holocellulose

The procedure for holocellulose and alpha-cellulose content determination was adapted from Zobel et al. (1996).

0.3-0.5g of air dried extractive-free sample was weighted into a 125ml of Erlenmeyer flask and the weight was noted. Into the flask, 32ml of distilled water, 0.1ml glacial acetic acid and 0.3g of sodium chlorite were added subsequently. The flask was then loosely covered by an inverted 10ml Erlenmeyer flask and placed in a
water bath at a temperature of 70-80°C. After one hour of cooking and occasional swirling, another 0.1ml of acetic acid and 0.3g of sodium chlorite were added to the flask while it was in the water bath. The content was continued to cook for an additional hour. The third addition of acetic acid and sodium chlorite was repeated for the third hour. After another hour, the flask was placed in an ice bath to cool to below 10°C. The content in the flask was then filtered through a known-weight glass Gooch crucible with coarse porosity fitted disc. Ice cold distilled water was used to rinse and transfer the residue in the flask. The content was then washed with hot distilled water followed by an acetone wash while under suction. The crucible was then dried at 105°C for 24 hours before weighing.

Holocellulose content was calculated by subtracting the weight of crucible from the final overall weight then divided by the original sample weight corrected with moisture content.

6 samples were prepared in total. 3 of them were dried in the oven for holocellulose determination and the other 3 were left out to dry at room temperature for alpha-cellulose determination.

**Alpha-cellulose**

Crucible containing the holocellulose prepared from the previous section was placed in a water bath at 20±5°C. The water level was controlled so that it just reached the fitted filter disc. 3ml of 17.5% (w/v) sodium hydroxide was added and the mixture was macerated with a glass rod for 1 minute. Subsequently, 2ml of the 17.5% sodium hydroxide was pipetted and macerated for 45 seconds follow by another 2ml addition and 15-second maceration. The mixture was left to stand for 3 minutes. Next, 2ml of the 17.5% sodium hydroxide was added followed by three 2ml additions at the end of 2.5 minutes, 5 minutes and 7.5 minutes. In total, 15ml of 17.5% (w/v) sodium hydroxide was put into the crucible. The crucible was covered and left in the water bath for 30 minutes. 20ml of distilled water was then added and an additional 30 minutes was spared for the crucible to stand in the water bath. The content in the crucible was filtered under suction and rinsed with five successive 50ml of hot water to rinse out the chemicals. The crucible was then filled with 2N
nitric acid and left to stand with no suction for 5 minutes. At the conclusion of the 5 minutes, the acid was filtered out first and then the contents were washed with distilled water until the pH was neutral. The crucible was then dried at 105°C in oven and weighted.

Alpha-cellulose content was calculated by subtracting the weight of crucible from the final overall weight then divided by the original sample weight corrected with moisture content. Hemicelluloses content was the difference between the holocellulose and alpha-cellulose content.

**Klason lignin and acid soluble lignin**

Klason lignin and acid soluble lignin contents were measured based on the procedure described in TAPPI T 222 om-06 and T 250 um-94.

0.3-0.5g of extractive free sample was accurately weighted into a 50ml Erlenmeyer flask and the weight of sample was noted. Into the flask, 15ml of chilled (4°C) 72% (w/w) sulphuric acid was added. The flask was covered with parafilm and swirled manually for a minute or so to ensure sufficient wetting between the acid and the sample. The flask was placed on a shaker operating at low speed for 2 hours.

At the conclusion of the 2-hour period, the content in the flask was transferred into a 1L Erlenmeyer flask and 560ml of distilled water was added to dilute the acid concentration to 3%. The new mixture was left to boil for 4 hours on a hot plate while maintaining the fluid level at 575ml. The solution was then allowed to cool down over night and filtered through a known-weight glass Gooch crucible with medium porosity fitted disc. 15-20ml of the filtrate was collected for acid soluble lignin content determination. The residue in the Gooch crucible was subsequently washed with 500ml of hot distilled water. The crucible was oven-dried at 105°C for 24 hours and weighted.

Klason lignin content was calculated by subtracting the weight of crucible from the final overall weight then divided by the original sample weight corrected with its moisture content.

To determine the acid soluble lignin concentration, the filtrate collected previously from the klason lignin measurement was filled in a 1cm light path cuvette
and measured for its absorbance at 205nm by a spectrophotometer using a 3% sulphuric acid as reference blank. The acid soluble lignin was calculated according to Beer’s law as

$$\text{% AcidSoluble Lignin} = \left( \frac{\text{Absorbance}}{\varepsilon b} \right) \times \frac{0.575L}{\text{Oven dry weight of sample}} \times 100\%$$

where $\varepsilon$ is the molar absorptivity of 3% sulphuric acid and $b$ is the path length of the cuvette. The values for these two parameters were 110 L/g/cm and 1cm respectively.

3.2.2.3 Degree of Polymerization

Bleached wheat straw pulp and pulp processed under different conditions from Set A to Set D were tested for degree of polymerization (DP).

DP was obtained by measuring the intrinsic viscosity of the fibre containing cupriethylenediamine (CED) solution in a calibrated glass capillary-type viscometer according to ASTM D1795-96 and TAPPI 230 om-94 standards. The intrinsic viscosity test is a simple and sensitive way to indicate the average fibre length change caused by degradations of cellulose from the action of chemical and mechanical treatment (Lapierre et al. 2006).

The following method was adapted from the ASTM D1795-96 and TAPPI 230 om-94 standards. A calibrated Cannon-Fenske routine viscometer in ASTM size 100 was employed in this test.

Due to the hornification phenomenon caused by drying, nanofibre-water suspension with known consistency, around 0.5%, was tested rather than the oven dried sample to facilitate dissolution. Each sample suspension was weighted and added to a bottle containing 25ml of 1M CED solution. The weight of suspension added was calculated to contain 25ml of water in order to dilute the final CED solution to 0.5M.

The mixture was then topped with nitrogen to prevent oxidation and shaken to disperse the fibre. The dissolution time of fibre in CED solution has an impact on the intrinsic viscosity. Once the fibres are fully dispersed in the solution, prolonged
standing in the CED solution can lead to fibre degradation and influence the results (Lindsley 1951; Browning 1967). Therefore, the measurement was taken 60±5 minutes after mixing for every sample to allow sufficient dissolution time and to generate comparable data.

When the solution was ready, the viscometer was filled by immersing its small diameter leg into the solution and drawing the solution into the instrument by applying suction to the other end. The solution was drawn to the second etch mark. The viscometer was then returned to its vertical position and placed in a constant-temperature water bath at 25°C for at least 5 minutes. The solution was drawn into the measuring leg with a sucking bulb until the liquid level passes the etch mark between two bulbs. The efflux time, t, required for the meniscus to pass from the top to the lower etch mark was measured with a stop watch. The measurement was repeated for two times and the average was used in the calculation. In the same way, the efflux time for 0.5M CED solution, t₀, was determined. The relative viscosity, η_rel, was calculated as follows,

\[ \eta_{rel} = \frac{t}{t_0} \]

The intrinsic viscosity, \([\eta]\), was then corrected with the fibre concentration in the mixed solution, c, in the unit of g/dL,

\[ [\eta] = [\eta] \times c / c \]

where the product, \([\eta] \times c\), was obtained in correspondence with \(\eta_{rel}\) from Table 3 in ASTM D1795-96.

DP of each sample was determined by multiplying the intrinsic viscosity, \([\eta]\), with a constant of 190 (Browning 1967).

3.2.2.4 X-Ray Diffraction

Crystallinity index of raw wheat straw, wheat straw after each chemical treatment step and samples from Set A to Set D were measured using an X-ray diffractometer (XRD/X’pert Powder, PANalytical) equipped with CuKα radiation in step-scan mode.
For raw wheat straw and chemically treated wheat straw (post-alkaline and bleached), the dried samples were firstly ground in a Wiley mill equipped with a 60 mesh sieve and then further screened through a 350 mesh sieve. However, for the mechanically treated samples, the size of fibres was significantly smaller and more hydroxyl groups were exposed at the fibre surface. Thus, after drying the mechanically treated pulps, it was then hard to grind them to such a small size. Therefore, for samples from Set A to Set D, the fibre films were tested instead of their powder form. A film made from bleached wheat straw was also tested to check if different sample preparations would generate comparable results.

For powder samples, the powders were highly packed using a spatula onto a glass slide. The sample size was around 2cm by 1.5cm square and the thickness was around 1-2mm. For films, a 2cm by 4cm piece was cut out and typed onto a silicon slide. Silicon slide was used because the fibre films were quite thin and the X-ray would penetrate through the films. If an amorphous glass slide was used, it would interfere with the results.

The samples were then clamped on to the sample holder and scanned from 2θ = 10 to 30°. The crystallinity index, \( C_{RI} \), was determined by

\[
C_{RI} = \frac{(I_{002} - I_{am})}{I_{002}} \times 100\%
\]

where \( I_{002} \) is the peak intensity corresponding to cellulose type I, and \( I_{am} \) is the intensity corresponding to the amorphous fraction. A typical scan of cellulosic material usually consists two peaks. \( I_{002} \) corresponds to the 2\(^{nd}\) peak and \( I_{am} \) corresponds to the base between the two peaks. They are usually found at 2θ = 22.6° and 18° respectively (Segal et al. 1959).

3.2.2.5 Tensile Properties

Tensile test was performed to evaluate the strength of fibre film prepared from the suspension in sample Set A to Set D. The test was conducted on an automated materials testing system (Series IX, Instron Corporation) based on the procedure
described in ASTM D638.

The test machine was equipped with a 2KN capacity load cell. A span of 25mm was used and the crosshead moved at a speed of 2.5mm/min. The specimens were cut into a dog-bone shape according to the specifications of the type V specimen illustrated in the standard. At least five specimens were tested for each sample. The maximum strength, Young’s Modulus and strain to failure of the fibre films were evaluated.

There are two major factors that dictate the tensile properties of the sample, the thickness and the density of specimen. The maximum tensile strength is calculated by dividing the maximum load by the cross-sectional area of the specimen, and the Young’s Modulus is related in a more complex way. As the thickness of nanofibre films was very small, a precision micrometer (49-61, TMI, USA) was used to measure the thickness of the film by applying constant pressure. It could read up to 4 digits after the decimal point of a millimeter. The higher the density would also results in higher tensile properties as there are more fibres per unit area. The tensile properties of fibre films were reported along with their densities.

3.2.2.6 Optical Properties

Substrates that possess good optical properties are the foundation of transmissive displays. As filler, optical properties of nanofibre films are extremely important. Therefore, the regular light transmittance and refractive index of the films were tested.

**Light Transmittance**

The regular light transmittance of fibre films prepared from sample sets A to D was studied using a Cary 5000 UV-Vis-NIR spectrometer (Varian). The samples were placed on a solid sample holder and scanned in the visible wavelength range, 400-800nm. As smudging or grease on the film surface would greatly affect the % of light transmittance, the samples were gently wiped before testing. The sample holder gave a 1cm by 2cm window for scanning. A minimum of 2 scans were run for each
sample at different locations and the average value was reported.

Refractive Index

The refractive index, n, is one of the fundamental parameters of a material used in optical applications. The refractive index of a material is defined as the ratio of the velocity of electromagnetic wave traveling in vacuum (c) and to the phase velocity of the same wave in the material (v) (Palik 1998). Refractive index can usually be measured by a refractometer or an ellipsometer. The refractive index also has a direct relationship with the relative dielectric constant (εₖ) and the relative permeability (μₖ) of the material (Hayden 1909).

\[ n = \sqrt{\varepsilon_k \times \mu_k} \]

μₖ is very close to 1 for all except magnetic materials (Hayden 1909). Therefore, the refractive index equals to the square root of the relative dielectric constant.

The relative dielectric constant of fibre films made from set A to D was measured with assistant from Professor Hathaikarn at Chulalongkorn University in Thailand by using a precision LCR meter (E4980A, Agilent).

The dried samples were first covered by a coating of conductive silver paint on each side. Two probes that were connected to the LCR meter sandwiched the sample in between and measured the dielectric constant from the frequency of 10 to 10E06 Hz.

3.2.2.7 Thermal Properties

Thermal stability of the nanofibres was investigated by their degradation temperature and coefficient of linear thermal expansion.

Thermal Gravitational Analysis

Thermo gravimetric analysis (TGA) is a common technique to measure the mass of a sample as a function of temperature. Changes of mass occur during evaporation, decomposition, chemical reaction and so on. In the case of this study, the change of mass was mainly due to moisture evaporation from the fibre films and decomposition of the samples.
TGA data is affected by the form, dimension, density and mass of the specimen due to heat transfer principles, and the volatile matters initially presented, which in this case was moisture. For raw wheat straw and chemically treated samples, the specimens were prepared by grinding the oven dried material in a Wiley mill to 40 mesh size. For the nanofibres, hornification caused by drying made grinding very difficult. Therefore, the samples, A-30, B-10, Set C and Set D, were tested to check the impact of different mechanical treatments on thermal degradation. The suspensions were firstly solvent exchanged with ethanol. The ethanol suspensions were then dried at room temperature, and towards the end, the lumps were separated by hands. The less polar ethanol reduced the chance of hydrogen bonding formation during drying process resulted in a powder form. The specimens were kept in desiccator to prevent moisture absorption. Relatively same amount of specimens were tested. In the final product, the nanofibre film was used rather than the powder. Therefore, the films of these samples were also tested. However, due to their differences in thickness and density, it was hard to generate comparative data. Therefore, the average for these samples was reported.

The test procedure was based on ASTM E1131. A TGA Q500 model from TA Instruments was used to run the test from room temperature to 600°C with a heating rate of 10°C/min in a nitrogen environment. On-set degradation temperature, \( T_i \), was reported as the initial degradation temperature at the intersection of extrapolated starting mass with the tangent applied to the maximum slope of the curve. The temperature at the maximum weight loss rate, \( T_{\text{max}} \), was found in the differential TG curve, which measures the change in mass over change in temperature. The residue mass percentage was reported as well.

**Thermal Mechanical Analysis**

The change in dimension in certain direction without external forces as a function of temperature is defined as the coefficient of linear thermal expansion (CLTE) of a sample. CLTE can be measured with a dilatometer, such as a thermal mechanical analyzer (TMA). TMA test was conducted with the courtesy of GE Power and Water by using the TMA Q400 from TA Instruments. A 3mm by 25mm strip was
prepared for the B-10 fibre film. The test was run with a setup for films in the tensile mode. The span between the two clamps was set at 16mm. A heating ramp was used from 25°C to 120°C with a heating rate of 5°C/min in a helium environment. The average CLTE was reported in this temperature range in the unit of ppm/°C or ppm/K and was calculated by the dimensional change of the sample at certain temperature divided by the initial sample length.

3.2.3 Characterization of Acrylate Resins

Pure acrylate resins were characterized in terms of degree of cure, and tensile, thermal and optical properties. The samples were cured with 1% of PI1 and 0.1% of PI2 for 2 minutes on each side unless otherwise stated. The thickness of the resin was controlled at 0.5mm.

3.2.3.1 Degree of Cure

Extent of cure is an important property of radiation cured resins as undercure or overcure would impart detrimental properties to the composite. It is influenced by the molecular weight and functionality of the acrylate resins, photoinitiator concentrations and irradiation dosage (Rechel 1995). It can be evaluated by the degradation rate at certain elevated temperature or change in molecular weight.

Samples were prepared for Resin 1 and 3 only. The nanocomposite made with Resin 2 showed poor adhesion, therefore, its properties was not further pursued in this section. For Resin 1 and 3, they were cured for 1, 2 and 3 minutes on each side with 1 or 2% of PI1 and 0.1 or 0.2% of PI2. Thus, 6 samples were made for each resin. The resins were cured in a mold and the thickness was controlled at 0.5mm.

*Dynamic Mechanical Analysis*

Cross-link density can be indicated by the level of storage modulus, $E'$, in the rubbery plateau region above $T_g$ of a material according to Flory’s rubber elasticity theory. The cross-link density, $\nu_e$, defined as the number of moles of elastically effective network per volume, is calculated using the equation
\[
\nu_c = \frac{E'}{3RT}
\]

where \( R \) is the gas constant, 8.314 J/K/mol and \( T \) is the temperature in absolute temperature K, at which \( E' \) in the rubbery plateau region has reached (Hill 1997). This equation is valid when assuming the network formation is complete and there are no small loops or dangling ends. The ideal network is not always formed. Therefore, the equation is an estimation of the cross-link density. Nevertheless, \( E' \) is in proportional to the cross-link density. In other publications, cross-link density is also expressed as the molecular weight of the cured resin. This study followed Hill’s definition of cross-link density.

Swell test is a simple and low cost technique used widely in determining cross-link density, but the Flory-Huggins interaction parameter for the material in certain solvent is needed to calculate the cross-link density (Hansen 1995). Since the molecular structure and weight, and this parameter are unknown, by doing swell test, the final calculation of cross-link density would also be an estimation.

Due to simplicity and accuracy, the storage modulus method was used in this study.

Dynamic mechanical analysis (DMA) applies a minor oscillation force to a sample to yield information of its storage modulus. DMA Q800 from TA Instruments was used for the test. A strip of cured sample in the dimension of 30mm by 6mm was clamped with a controlled torque screw driver on to the tension clamps. An oscillation frequency of 1 Hz was used and a 0.05N of force was applied to the sample. A heating ramp was run from 30°C to 120°C with air as purging gas. The \( E' \) of Resin 1 was reported at 60°C and 100°C for Resin 3. Two samples for Resin 1 and 3 cured at different photoinitiator concentration and different curing duration was tested and the average was reported.

**Thermal Gravitational Analysis**

Samples with higher cross-link density are expected to be less susceptible to oxidation because of reduced mobility of radicals, slower volatiles evaporation and segmental mobility (Krongauz and Ling 2009). Polyacrylates degrade through
decarboxylation thus form carbon dioxide, acrylate monomers and alcohols. Depends on the medium, the decomposition go through either bond scission in oxygen or hydrogen abstraction in other medium.

The thermal degradation of cured Resin 1 and 3 was studied by aging the samples at 300°C for 60 minutes. At 300°C, both cured reins were started to degrade. By holding the temperature at this level helped to accelerate the oxidation process. Samples were cut using a hole punch so that they were uniform in size. The same TGA was used as in section 3.2.2.7 (TGA Q500, TA Instruments). The machine was firstly equilibrated at 30°C, then ramped with a heating rate of 20°C/min to 300°C and held for 60 minutes isothermally. The test was conducted in a nitrogen environment.

3.2.3.2 Tensile Properties

Tensile properties of cured Resin 1, 2 and 3 were tested. The testing procedure was based on ASTM D638 and described in detail in section 3.2.2.5.

3.2.3.3 Thermal Properties

Tensile properties of cured Resin 1, 2 and 3 were tested. The degradation temperature was determined based on the procedure outlined in section 3.2.2.7. The samples were cut using a hole punch for uniform size.

Glass transition temperature, Tg, is the mark of non-crystallined materials changing from a glassy state to a rubbery state. The mobility of chain segments is greater above the Tg than it is below it. Due to this fact, a step-like change would occur in the specific heat capacity (Ehrenstein et al. 2004). Differential scanning calorimetry (DSC) which measures the change in heat flow verses temperature could locate Tg. Tg is a basic property of polymers and it was important in the case of this study for the DMA analysis as the rubbery plateau can only be reached after passing Tg. Knowing the Tg, would be beneficial to decide the testing range for DMA.

ASTM D 3418 describes the procedure of using DSC to determine Tg. DSC Q1000
from TA Instruments was employed to run the test. Around 10mg of sample was tested for all resins. Duplicate heating run was conducted on the samples in nitrogen environment. The first heating run revealed the thermal and mechanical history of the sample and it is generally not suggested for property assessment (Ehrenstein et al. 2004). With controlled cooling, the samples was returned to the initial temperature and then heated for the 2\textsuperscript{nd} time. The heating and cooling rate were 20°C/min and the test was run from -80°C to 200°C. The upper temperature limit should not exceed the decomposition temperature. As shown from the results of TGA analysis, 200°C was well below where the resins started to degrade. Two tests were run for each sample and the averaged midpoint T\textsubscript{g} was reported, where half of the change in specific heat capacity has occurred.

3.2.3.4 Optical Properties

Regular light transmittance and refractive index were examined for pure Resin 1, 2 and 3. The test procedures followed the ones illustrated in section 3.2.2.6.

3.2.4 Characterization of Nanocomposite Films

Nanocomposite made with B-10 fibre film and different acrylate resins were prepared for characterization. The samples were cured with 1% of PI1 and 0.1% of PI2 for 2 minutes on each side.

3.2.4.1 Tensile Properties

Tensile properties of the nanocomposites with different fibre loading were tested according to the procedure described in detail in section 3.2.2.5.

3.2.4.2 Optical Properties

Regular light transmittance was tested following the procedure outlined in section 3.2.2.6.
3.2.4.3 Thermal Properties

Thermal degradation profile was run by TGA for the nanocomposites with different fibre loading. The samples were cut using a hole punch for uniform size. A ramp method was used with a heating rate of 10°C/min from room temperature to 600°C. CLTE was also measured according to procedures described above.

3.2.4.4 Bending Test

Flexibility is the ability of the composites to be bent or flexed without cracking or undergoing other failure. This feature is particularly important as the goal of this project was to create flexible and foldable composite films.

To date there has been very little published work on testing protocols, especially for flexible substrate with coated barrier and conductive layers (MacDonald 2004). In the study conducted by Gorkhali et al. 2003 and Bouten 2002, the bending test of a sample was conducted either on a repetitive 3-point bending system or with a pair of automatic arms that moves close and away from each other with sample laid flat in between the two arms.

However, the nanocomposite in this study was not robust and structured enough to be tested in such ways described above. Therefore, the bending property of the composite was assessed by bending the nanocomposite manually over the device illustrated in Figure 2 back and forth for 1000 cycles to mimic the bending and rolling in real life situation.

![Illustrative diagram of bending test fixture.](image)

Figure 2 Illustrative diagram of bending test fixture.

Two 1-inch diameter copper tubes were securely bound together with rubber
bands. The composite was inserted in between the two tubes. One end of the composite was wrapped around one of the tubes and taped to the position where the center axis of the composite meets the contact point of the copper tubes. When the composite was bended towards the taped end, an “O” shape was formed to mimic rolling action; when the composite was bended backwards, an “S” shape was formed to mimic arbitrary bending action.

After 1000 cycles, the composite was visually evaluated to check if there was any stress-whitening zone at the center axis. The light transmittance around the center axis was also measured. The composite was then cut into 5 type-V specimens described in ASTM D638 against the center axis and tested for tensile properties. The tensile test was targeted to see whether the bending had caused any weak points at the center. Therefore, not only the values were important so were the positions at break.

3.2.4.5 Abrasion Test

The surface durability of a composite is usually evaluated by abrasion resistance test. For a flexible substrate that would be applied to make portable devices, abrasion test can reveal sample’s resistance to daily wear and tear. There are two general forms of abrasion, marring and wearing, which are the permanent deformation and removal of material on the surface of the composites by mechanical forces respectively (Morse 1995). Mar resistance test is utilized to measure the ability of the composites to withstand scratching, scuffing and denting actions which tend to deform the surface appearance (Guévin 1995).

Abrasion test was conducted based on the ASTM D1044-08 which test for resistance of transparent plastics to surface abrasion. A Taber Model 5150 abrader (Taber Industries) was used with a CS-10 abrasion wheel attached. CS-10 is a medium to mild abrasion wheel designated to simulate the abrading action like that of normal handling, cleaning, and polishing. It is used to evaluate abrasion resistance of coatings, plastics and leather products (www.taberindustries.com). 500g weight was
put on the abrasion wheel during testing. For B-10 and Resin 1/Resin 3 nanocomposites, 100 abrasion cycles were used according ASTM.

3.2.4.6 Thermal aging

The nanocomposites made with B-10 fibre film and Resin 1 and Resin 3 were conditioned at 70°C in a convection oven for 7 days. Then, the composites were tested for tensile, optical and thermal properties, and discoloration.

Tensile test, thermal degradation temperature measured by TGA and light transmittance were conducted in the same manner described in previous sections.

Discoloration was tested to observe if there would be any yellowing caused by thermal aging. The test was done by using a portable spectrophotometer (CM-2002, Minolta). The device measure the color of the composite prior to and after the aging based on the CIE 1976 (L*, a*, b*) color space (CIELAB) specified by the International Commission on Illumination in year 1976. The three coordinates, L*, a*, b*, represents the lightness, chromaticity in between the color red and green, and chromaticity in between the color blue and yellow respectively (HunterLab 2008a). The 3-dimensional model is best illustrated in the Figure 3.

![Illustrative CIELAB color space.](image)

A change in the coordinates would indicate discoloration. Due to the fact that the nanocomposites were highly transparent, LAB values were tested against the calibration background provided along the portable color device for consistency.
Chapter 4  Results and Discussion

4.1  Effect of Chemical and Mechanical Treatments on Fibre Properties

After a series of chemical treatments and mechanical defibrillation, wheat straw had transformed from its original state to nano-scaled fibrous form. During the treatments, not only the chemical composition of the material changed, but also its physical properties. In this section, the characterization results of wheat straw at different stages were presented and discussed.

4.1.1  Fibre Morphology

Morphology of wheat straw fibres after different types and cycles of mechanical defibrillation was analyzed by TEM. The images of fibres were taken with 35K magnification.

Figure 4 exhibited samples from Set A while Figure 5 displayed samples from Set B. Samples from these two sets were solely processed mechanically in the high shear defibrillator for 50 and 20 passes respectively. Set A was a test run for inspection.

A great amount of inorganic substances were observed mostly in Set A samples. Inorganics behave different under the electron beam and have higher contrast comparing to organic substances. They appeared as black dots in the TEM images and were from the surface of the defibrillator since Set A was the first set of samples run through the machine. This was directly linked to the thermal degradation analysis of A-30 sample as its percentage of residue at end of the heating cycle was much higher than the others. An image of a spherical cluster of inorganic substances was presented in Figure 4(f). Once the impurities were worn away after frequent uses, fewer dots were observed in the images of other sample sets. Also, after many usage, the optimal operation condition was found and improved the defibrillation efficiency.
**Figure 4** TEM images of Set A (defibrillator batch 1) samples.
Bleached wheat straw pulp had visible large diameter fibres. In Set A, after 10 passes, smaller diameter fibres appeared to separate off from the micro-sized fibre bundles. With further processing, nanofibres became more individualized and obvious from the TEM images. The diameters of these nanofibres were mostly around 10-25nm and occasionally a few larger diameter fibres were observed.

Set B samples were processed a few months apart for Set A. The inorganic substances were mostly cleared from the samples. For every 10 passes, a sample was collected. Since the efficiency of the defibrillator had been improved and by confirming with the degree of polymerization (DP) and tensile proprieties, B-10 was the optimal sample for this set, while A-30 was the one for Set A.

The fibre samples processed by the high shear defibrillator had more uniform diameters but poor dispersion. As show in Figure 4(c) and (d), the bigger fibres were smeared and single nanofibre strands were appearing. However, they remained connected with adjacent nanofibres in a bundle form. The condition was even more obvious in Figure 4(c) where the nanofibres looked like a bunch of hair. Without the aid of microscope, the bundle would appear like a regular fibre to naked eyes. This was not the ideal case as there must be some points connecting the strands together. At these points, the apparent diameter must be larger which may cause reduction in transparency if the diameter exceeds the visible wavelength range. In addition, high strength of nanofibre film mainly came from the hydrogen bonding and the interweavement between fibres. If the fibre strands were in one direction, there would be less interaction between them, thus reduces the strength.

Likewise, if the aspect ratio of fibres decreased, so would the strength of the fibre film. Once passed the optimal process cycles, 30 for Set A and 10 for Set B, fibres must had undergone some sort of degradation that caused the tensile properties to go down. Under the same magnification, in the images taken for the samples before the optimal cycles, it was hard to find the ends for each fibre, but with fibres that had been over processed, fibre ends were easily found in the corresponding images. This indicated that the fibre length had been reduced. This phenomenon was more visible for sample B-20, where the image showed cloudiness.
and the fibres on the right hand side had much shorter length.

**Figure 5** TEM images of Set B (defibrillator batch 2) samples.

![Figure 5 TEM images of Set B](image)

**Figure 6** TEM images of Set C and D (homogenized) samples.

Images for fibres processed by the high pressure homogenizer, Set C and Set D, were shown in **Figure 6**. Set D was solely process by homogenizer. The fibre diameters were significantly larger and lacked uniformity compare to the other sets, but the fibres looked more separated from each other. With the aid from the defibrillator, Set C appeared to have similar diameter observed in Set A and B and fibre dispersion was improved.
The difference between the high shear defibrillator and high pressure homogenized samples might be caused by the different forces generated in these two machines. The defibrillator generates shearing force that smashed the fibres and forced them to separate. The high pressure homogenizer generates mainly impact force which may burst fibres to become more individualized but not sufficiently enough to initiate the separation itself.

The majority of fibres from Set A, B and C had diameter around 10-25nm, while for Set D, the fibre diameter was around 30-50nm. Reported by Abe and Yano (2009), bleached wood and rice straw pulp had diameter ranges of 12-20 and 12-35nm respectively after one pass through the Super Masscolloider.

Worth to point out was that despite that TEM was an explicit tool to study fibre morphology, the findings may not be conclusive and representative due to the view limit and sample preparation. Moreover, even when nanofibres were individualized, they tended to aggregate and the size of the agglomerate sometimes occupied a few grids. At this high magnification, the microscope could only survey the border of the agglomerate to get a clear shot. The assumption was that the fibres at the border had larger diameters than the ones within the agglomerate. Fibres aggregate because of the hydrogen bonding formed with adjacent fibres when the dispersion media, water, was taken away during sample preparation. Fibres with larger diameter would have less surface area than the ones with smaller diameter, thus, fewer sites for hydrogen bonding formation and less affinity with the other fibres. Therefore, they would tend to stay around the border of the agglomerate. This assumption was based on the author’s observations at the sites where available that showed fibres within the agglomerate had smaller diameters as displayed in Figure 7. Images in Figure 7 were taken at 100k magnification for sample A-30 and B-20. A large pile of material would not show its morphology under a TEM as the beam could not pass through. A scanning electron microscope (SEM), which only looks at the surface properties, might be a good way to image larger quantity of fibres in their film form to assess the fibre diameter distribution.
Figure 7 TEM images of sample A-30 and B-20 at 100k magnification that had shown smaller diameter fibres exist inside the agglomerates.

With all being said, even though the images taken were from samples that had been processed differently, the fibre conformations observed in each image had the chance to be presented in all of the samples rather than one. The decreasing trend in fibre diameter with more processing, however, was distinct. This was also consistent with the DP results. The author tried to give the most representative image for each sample.

4.1.2 Chemical Compositions

Chemical compositions of raw, alkaline treated and bleached wheat straw are listed in Table 3.

Extractives content presented in raw wheat straw was slightly high comparing to 8% sited in literature (Enayati et al. 2009). This might be caused by the fact that the wheat straw were not freshly collected. The alpha-cellulose, hemicellulose and total lignin contents of raw wheat straw were comparable to Alemdar and Sain (2008).

The function of NaOH was to swell the wheat straw, increase the surface area, solubilize lignin and hemicellulose. After NaOH treatment, the total lignin content had dropped from 16.8 to 12% and the hemicellulose content had decreased from 31.1 to 11.4%.
Bleaching wheat straw with NaClO₂ was aimed to remove lignin. There was 1.3% of total lignin content left after bleaching with relatively no change in other components if corrected to the same weight basis. 1.3% of total lignin content corresponds to a Kappa number of 9. ISO 9706 called the maximum Kappa number of permanent paper for documents was 5. The bleached wheat straw generated in this study would have lower brightness and a yellowish tint comparing to the printing paper due to the high Kappa number.

**Table 3** Percent chemical compositions of raw and chemically treated wheat straw (standard deviation based on n=3).

<table>
<thead>
<tr>
<th></th>
<th>Raw Wheat Straw</th>
<th>Alkaline Treated Wheat Straw</th>
<th>Bleached Wheat Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>11.1 (0.34)</td>
<td>2.32 (0.23)</td>
<td>-</td>
</tr>
<tr>
<td>Holocellulose</td>
<td>71.0 (2.25)</td>
<td>82.2 (0.65)</td>
<td>96.6 (0.86)</td>
</tr>
<tr>
<td>alpha-Cellulose</td>
<td>39.9 (0.45)</td>
<td>70.8 (0.75)</td>
<td>82.9 (0.28)</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>31.1 (2.30)</td>
<td>11.4 (1.00)</td>
<td>13.7 (0.91)</td>
</tr>
<tr>
<td>Total Lignin</td>
<td>16.8 (0.46)</td>
<td>12.0 (0.25)</td>
<td>1.29 (0.10)</td>
</tr>
<tr>
<td>Klason Lignin</td>
<td>15.1 (0.45)</td>
<td>10.9 (0.25)</td>
<td>0.26 (0.03)</td>
</tr>
<tr>
<td>Acid Soluble Lignin</td>
<td>1.71 (0.10)</td>
<td>1.09 (0.03)</td>
<td>1.03 (0.09)</td>
</tr>
</tbody>
</table>

Iwamoto et al. (2008) stated that hemicellulose serves as inhibitors to hornification, contributing to the ease of defibrillation. However, high hemicellulose and lignin contents would have an adverse effect on the tensile properties of the final fibre film as they are amorphous in nature.

Chemical composition of mechanically treated pulp was assumed to stay constant as there were no further chemical reactions. Some water soluble components might be washed out, but the amount was assumed to be negligible.

### 4.1.3 Degree of Polymerization

The DP of bleached wheat straw and samples from Set A to D are listed in Table 4 below. In addition, the wheat straw nanofibre produced using the same method as Alemdar and Sain (2008) was also measured for comparison.
Table 4 Intrinsic viscosity and degree of polymerization of defibrillated fibres.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Efflux Time</th>
<th>Relative Viscosity</th>
<th>Fibre Concentration</th>
<th>Intrinsic Viscosity</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M CED (t₀)</td>
<td>74.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleached</td>
<td>852</td>
<td>11.5</td>
<td>3.58</td>
<td>0.30</td>
<td>11.9</td>
</tr>
<tr>
<td>A-10</td>
<td>347</td>
<td>4.68</td>
<td>2.01</td>
<td>0.20</td>
<td>10.3</td>
</tr>
<tr>
<td>A-20</td>
<td>361</td>
<td>4.87</td>
<td>2.08</td>
<td>0.27</td>
<td>7.73</td>
</tr>
<tr>
<td>A-30</td>
<td>227</td>
<td>3.06</td>
<td>1.37</td>
<td>0.18</td>
<td>7.57</td>
</tr>
<tr>
<td>A-40</td>
<td>229</td>
<td>3.09</td>
<td>1.38</td>
<td>0.19</td>
<td>7.31</td>
</tr>
<tr>
<td>A-50</td>
<td>238</td>
<td>3.22</td>
<td>1.44</td>
<td>0.21</td>
<td>6.75</td>
</tr>
<tr>
<td>B-10</td>
<td>337</td>
<td>4.55</td>
<td>1.97</td>
<td>0.30</td>
<td>6.50</td>
</tr>
<tr>
<td>B-20</td>
<td>287</td>
<td>3.87</td>
<td>1.72</td>
<td>0.30</td>
<td>5.70</td>
</tr>
<tr>
<td>Set C</td>
<td>258</td>
<td>3.48</td>
<td>1.55</td>
<td>0.31</td>
<td>5.09</td>
</tr>
<tr>
<td>Set D</td>
<td>368</td>
<td>4.97</td>
<td>2.10</td>
<td>0.27</td>
<td>7.87</td>
</tr>
<tr>
<td>Alemdar and Sain</td>
<td>136</td>
<td>1.82</td>
<td>0.67</td>
<td>0.21</td>
<td>3.21</td>
</tr>
</tbody>
</table>

Bleached wheat straw showed the highest DP as their diameters were still in the micron range. For Set A, the DP dropped significantly for the first 20 passes, from 2259 to 1468. After that, there was only a minor decrease in DP. This was similar to Set B samples except that the big drop had happened within the first 10 passes as the efficiency of the defibrillator had improved. The drop in DP at the beginning was more related to the decrease in fibre diameter. As shown in the TEM images of these samples, the average fibre diameters had remained relatively constant after a few passes in the defibrillator. The minor change in DP at a later stage could be linked to mostly the decrease in overall fibre length and fibre-fibre separation.

As mentioned previously, 30 and 10 were the optimal processing cycles for Set A and B respectively. Samples processed beyond that point were considered overprocessed as the properties of fibre films started to decrease. DP of B-10 was slightly lower comparing to the over-processed A-50, but its tensile properties were much higher. The reason for that was A-50 was affected by the presence of inorganic substances. Henriksson et al. (2008) also showed that nanofibre films with higher DP would result in better tensile properties.

The firstly defibrillated then homogenized Set C showed a DP below 1000. The
additional 10 passes in the high pressure homogenizer had more impact on the DP than the 10 passes in the defibrillator (B-20). Besides the chance of shortened fibre length, decrease in DP may mainly due to the better fibre-fibre separation. DP of Set D was quite high, 1495, even though the sample had been processed for 50 cycles. This was mainly owing to the larger diameter of fibres.

Sample prepared using the method described in Alemdar and Sain (2008) had the lowest DP among all. This was because of the application of a more aggressive mechanical treatment during the defibrillation process. The average diameter of the fibre was reported to be 30-40nm which was similar but higher as compared to the results from the proposed process. The decrease in DP may have more correspondence with the decrease in fibre length, and thus aspect ratio and tensile properties of the nanofibre.

In the previous work by Iwamoto et al. (2007), bleached wood pulp was used and processed in a Super Masscolloider for 0-30 times. The DP dropped from 760 initially to 400 after 30 passes through the defibrillator. The fibre diameter was in the range of 15-25nm. Zimmermann et al. (2010) had studied nanofibres processed by Microfluidizer from different raw materials. The DP of unprocessed soft wood, wheat straw and beech wood pulp were 2249, 1433 and 1088 respectively, then decreased to 825, 794 and 930 respectively after the Microfluidizer.

### 4.1.4 Degree of Crystallinity

Crystallinity index was calculated from X-Ray diffraction (XRD) pattern using Segal’s method (Segal et al. 1959). For raw, alkaline treated and bleached samples, their powder form was tested while for mechanically treated fibres, the film form was used. Figure 8 showed the XRD patterns for the chemically treated wheat straw. The mechanically treated samples displayed similar patterns differ only in the peak intensities.
Crystallinity index of all samples tested are listed in Table 5. A film form sample for the bleached wheat straw was also tested to find out whether different sample preparations would have an impact on the result.

Table 5 Crystallinity indices of chemically and mechanically treated wheat straw. (Standard deviation based on n≥2)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Crystallinity Index</th>
<th>Sample ID</th>
<th>Crystallinity Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>51.9 (2.37)</td>
<td>A-40</td>
<td>68.1 (2.63)</td>
</tr>
<tr>
<td>Alkaline Treated</td>
<td>60.6 (3.06)</td>
<td>A-50</td>
<td>69.3 (3.41)</td>
</tr>
<tr>
<td>Bleached (Powder)</td>
<td>64.5 (2.18)</td>
<td>B-10</td>
<td>71.3 (3.99)</td>
</tr>
<tr>
<td>Bleached (Film)</td>
<td>68.3 (4.31)</td>
<td>B-20</td>
<td>70.7 (1.42)</td>
</tr>
<tr>
<td>A-10</td>
<td>68.1 (4.37)</td>
<td>Set C</td>
<td>71.4 (1.56)</td>
</tr>
<tr>
<td>A-20</td>
<td>69.3 (1.56)</td>
<td>Set D</td>
<td>72.2 (3.36)</td>
</tr>
<tr>
<td>A-30</td>
<td>69.5 (2.12)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Crystallinity index of chemically treated wheat straw had increased along the process. This was because a large quantity of amorphous hemicellulose and lignin had been eliminated. The powdered and film form of bleached wheat straw showed similar numbers with the latter one being slightly higher. However, the results were comparable if the standard deviation was taken into account.

After bleaching, there should not be much change in degree of crystallinity as
there were no further reactions. Nevertheless, the mechanically treated wheat straw had shown higher values of crystallinity index. Abe and Yano (2009) stated that the degree of crystallinity of bleached wood pulp increased from 71% to 79% after mechanical defibrillation. This trend was also reported in the study of Jonoobi et al. (2009) and it was attributed to the change in cellulose structures by the authors. Iwamoto et al. (2007) reported that the degree of crystallinity had decreased as the number of grinding passes increased due to mechanical degradation. However, this situation was not observed in the case of this study.

Degree of crystallinity is one of the key factors that determine the mechanical properties of nanofibres (Abe and Yano 2009). Increase in crystallinity also decreases cellulose’s chemical reactivity, ability to regain moisture and elongation (Ward 1950).

### 4.1.5 Mechanical Properties of Fibre Films

Tensile strength, Young’s modulus and strain to failure of the fibre films were reported in Table 6. At least 5 specimens of each sample were tested and the standard deviations were reported in parenthesis. The values were presented along with the densities of the films as their tensile properties were heavily dependent on the densities.

**Table 6** Tensile properties of fibre films from Set A to Set D. Standard deviations are given in parenthesis with n≥5.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Density (g/cm³)</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Strain to Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-10</td>
<td>1.26</td>
<td>135 (12.8)</td>
<td>9.34 (0.44)</td>
<td>3.36 (0.48)</td>
</tr>
<tr>
<td>A-20</td>
<td>1.23</td>
<td>161 (13.7)</td>
<td>11.4 (0.69)</td>
<td>3.24 (0.50)</td>
</tr>
<tr>
<td>A-30</td>
<td>1.27</td>
<td>176 (12.9)</td>
<td>12.4 (0.71)</td>
<td>3.78 (0.56)</td>
</tr>
<tr>
<td></td>
<td>1.51</td>
<td>204 (11.5)</td>
<td>13.9 (0.89)</td>
<td>3.52 (0.44)</td>
</tr>
<tr>
<td>A-40</td>
<td>1.24</td>
<td>167 (17.6)</td>
<td>11.6 (0.56)</td>
<td>2.8 (0.41)</td>
</tr>
<tr>
<td>A-50</td>
<td>1.23</td>
<td>153 (12.9)</td>
<td>11.3 (0.73)</td>
<td>2.76 (0.28)</td>
</tr>
<tr>
<td>B-10</td>
<td>1.26</td>
<td>181 (4.87)</td>
<td>11.75 (0.55)</td>
<td>2.95 (0.42)</td>
</tr>
<tr>
<td>B-20</td>
<td>1.34</td>
<td>169 (15.6)</td>
<td>10.5 (0.71)</td>
<td>3.12 (0.41)</td>
</tr>
<tr>
<td>Set C</td>
<td>1.29</td>
<td>188 (7.66)</td>
<td>11.93 (0.58)</td>
<td>2.96 (0.33)</td>
</tr>
<tr>
<td>Set D</td>
<td>1.28</td>
<td>140 (10.8)</td>
<td>10.4 (0.43)</td>
<td>3.36 (0.48)</td>
</tr>
</tbody>
</table>
The tensile strength and Young’s modulus of Set A samples raised by the number of passes in the defibrillator until 30 passes and then started to decrease. The increase was due to the isolation of the nanofibres, which eliminated the weak point existing between fibres, improved interfibril adhesion, and made the defects in the specimen smaller and more homogeneously distributed. The drop could be caused by over processing where the length of the fibre was cut short as shown in the TEM images.

Similar trend was found in Set B samples, only that the optimal number of passes had reduced to 10 as the efficiency of the defibrillator had improved. B-10 sample had tensile strength close to A-30 sample at same density. But the Young’s modulus was about 8% lower. As for Set B, only 2 samples were drawn for every 10 passes. There was the possibility that the optimal processing cycles may lie before or after 10. The small standard deviation was a good sign of homogeneousness throughout the sample.

Improved tensile properties of Set C sample, which was made from B-10 sample processed further through high pressure homogenizer, might suggested that B-10 was not over processed. However, the improved fibre dispersion could also have contributed to the higher tensile strength and Young’s modulus.

The poor results of the homogenized Set D sample were affected by the larger fibre diameter and inadequate uniformity which produced weaker fibre-fibre network.

When the density of the fibre film for sample A-30 increased from 1.27 to 1.51g/cm$^3$ by putting 20kg of weight rather than 10kg on top of the film while drying, the strength and Young’s modulus also went up almost proportionally. This was quite straightforward since more numbers of fibres were presented per unit volume that created stronger films. As the density for pure cellulose crystallite was 1.59 g/cm$^3$, it implied that the cavities in the films had almost been completely removed and these could be the ultimate tensile properties for A-30 (Nogi et al. 2009).

The strain to failure remained relatively constant for all samples. It suggested
that the films were rather brittle. The strain to failure did drop noticeably for the samples that were considered over-processed. Henriksson et al. (2008) concluded that the average molecular weight of nanofibres, i.e. DP, was directly linked to the strain to failure. Lower the DP, lower the percentage of elongation.

The nanofibre films prepared from rice straw derived nanofibres had tensile strength and Young’s modulus of 230MPa and 11GPa respectively with density of 1.36g/cm$^3$ (Abe and Yano 2009). Ishikura et al. (2010) studied the effects of treating dried nanofibre films with alkaline solution of different concentration. The results showed that with NaOH concentration higher than 10%, it could increase the strain at yield yet retain the strength by lowering the crystallinity of the fibre films. Henriksson et al. (2008) had reported the tensile strength and Young’s modulus of nanofibre films prepared from softwood to be 214MPa and 13.2GPa with density of 1.08g/cm$^3$ and strain to failure of 10.1%. Lindstrom (2007) obtained nanofibres by defibrillating wood pulp through a Microfluidizer and reported tensile strength, Young’s modulus and strain at failure to be 220MPa, 16GPa and 12% without disclosing the density. Lindstrom (2007) also indicated that the sample failure was more correlated to the debonding and slippage between nanofibres rather than the actual fibre failure. Therefore, good fibre dispersion and size uniformity were the necessary requirements to ensure uniform hydrogen bond distribution and excellent interweavement between fibres for better mechanical properties.

4.1.6 Optical properties of Fibre Films

4.1.6.1 Light Transmittance

Because of the light transmittance depends on the sample thickness and density, the light transmittance data was modified according to Beer-Lambert law in order to evaluate samples on the same basis. Beer-Lambert law states that the absorbance of a material equals to the product of molar absorbtivity, path length and concentration of the material. The absorbance equals to the $\log_{10}$ of 1 over percentage of light transmittance. The path length here was the thickness of the films. The
concentration could not directly correct with sample density. It represents the amount of testing material in the reference media, air in this case. As the baseline was measured by shooting the beam through the void on the sample holder, the volume was unknown. Since the sample density remains relatively the same, 1.23 to 1.34 g/cm$^3$, the light transmittance was only corrected with sample thickness. The corrected data used B-10 sample as reference, which had density and thickness of 1.26 g/cm$^3$ and 39 μm.

*Figure 9* plotted the percentage of regular light transmittance of each sample versus the wavelength.

![Figure 9](image.png)

*Figure 9* Regular light transmittance over visible wavelength of fibre films.

As the graph clearly laid out, the ranking in percent of light transmittance of each film corresponded nicely to their ranking in terms of degree of polymerization (DP), except for Set D sample. Set D had DP around the same as A-20 and A-30, but the light transmittance was much less because there were still a lot of large diameter fibres presented. For Set A samples, there was only slightly further improvement in light transmittance after 20 passes in the defibrillator, while B-10 and B-20 showed minor differences. Set A samples were less transparent compared to Set B samples.
due to two reasons. Firstly, there were many inorganic particles from the defibrillator which might have reflected or absorbed some of the light beam. Secondly, larger diameter fibres were found in Set A samples due to poor defibrillation efficiency.

Set C was the most transparent sample thanks to better fibre dispersion and uniform fibre diameters. There was almost a 50% improvement from Set B samples. The tensile strength of this sample was also the best when having a density close to 1.3 g/cm$^3$. However, this set was not chosen as the final verdict. Set C had very small DP that was below 1000. When making films with 0.3g of dry weight, the films at their wet stage were very delicate and it was hard to peel them off from the filter membrane without breakage. This could be caused by the better fibre dispersion that minimized the entanglement between fibres and since the sheet was still wet, the hydrogen bonds had not yet formed. To solve this problem, the dry weight of the film had to be increased to 0.4g. If assuming the density of the heavier weighted film was the same as before, the thickness or path length would increase by 25%. This reduced the film transparency from 36.6% to 18.3% at 800nm. Therefore, for the ease in nanofibre manufacturing and handling, Set C sample was not the best despite of their superior properties.

To be more explicit, the percent of light transmittance of fibre films at 400, 600 and 800nm wavelength were listed in Table 7.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% T at 400nm</th>
<th>% T at 600nm</th>
<th>% T at 800nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-10</td>
<td>8.92</td>
<td>13.4</td>
<td>16.9</td>
</tr>
<tr>
<td>A-20</td>
<td>10.0</td>
<td>15.5</td>
<td>20.3</td>
</tr>
<tr>
<td>A-30</td>
<td>10.0</td>
<td>15.9</td>
<td>20.5</td>
</tr>
<tr>
<td>A-40</td>
<td>10.4</td>
<td>16.2</td>
<td>20.8</td>
</tr>
<tr>
<td>A-50</td>
<td>9.8</td>
<td>16.0</td>
<td>21.2</td>
</tr>
<tr>
<td>B-10</td>
<td>12.2</td>
<td>18.7</td>
<td>24.2</td>
</tr>
<tr>
<td>B-20</td>
<td>12.6</td>
<td>19.4</td>
<td>25.0</td>
</tr>
<tr>
<td>Set C</td>
<td>20.9</td>
<td>30.1</td>
<td>36.6</td>
</tr>
<tr>
<td>Set D</td>
<td>6.21</td>
<td>7.32</td>
<td>11.0</td>
</tr>
</tbody>
</table>

The denser version of A-30, 1.51g/cm$^3$ rather than 1.27g/cm$^3$, showed light
transmittance of 6.8, 11.3 and 15.1% at 400, 600 and 800nm wavelength. Higher
density had an adverse effect on the transparency, although it could improve the
tensile strength. Therefore, there was a tradeoff between strength and transparency.

Another experiment was done on to evaluate the impact of surface smoothness
on light transmittance. Usually, the fibre film was dried with two 325 mesh nylon
clothes on each side to prevent it from sticking to regular filter papers. 325 mesh has
pores of 44 microns that are way bigger than the nanofibres. This could leave
patterns on the fibre film while it was drying. These patterns would roughen the
surface of the film and scatter more light, thus reduce light transmittance. To solve
this, the film was dried in between two filter membranes used for filtration. The pore
size of the membranes was only 0.1 micron. By taking this method, the light
transmittance of B-10 film improved dramatically to 25.9, 41.3 and 52.7% at 400, 600
and 800nm wavelength. The calculated density went up to 1.38g/cm$^3$, but there was
no improvement in terms of film tensile strength and even reduced light transmittance in the final composite. The reason for the higher density could also be
related to the surface roughness. The density of films was calculated by dividing the
weight of the film with measured film thickness times film area. The roughened
surface could raise the surface of the film and make the thickness appear larger. Thus,
there could be no change in the real density. The decrease in light transmittance of
the final composite could be due to the same reason. By coating fibre film with
acrylate resin, the resin would flow into and smooth out the surface defects of fibre
film which were prone to scatter light. Now, as the surface was smoother, the size of
voids in the nanofibre network had been reduced, which would prevent the resin to
flow in and repair the defects. This technique can be used when transparent
nanopaper was the desired product as it does not require as much polishing. In
conclusion, surface morphology had a great impact on the light transmittance. This
was more pronounced on the nanocomposite as any smudges or scratches could
reduce the light transmittance greatly.

In the work represented by Nogi et al. (2009), the nanofibre film prepared from
softwood pulp with thickness of 55 microns and density of 1.53g/cm$^3$ had a total light
transmittance of 21% at 600nm wavelength. The study used a 300 mesh when drying
the film.

4.1.6.2 Refractive Index

Refractive index (RI) indicates the speed of light in the interested material. Due
to scattering caused by surface roughness, the refractive index of fibre films could
not be measured using an ellipsometer or refractometer without polishing. Therefore,
the RI was approximated by the dielectric constant, which equals to the square of RI.
In literatures, RI of materials was usually reported at sodium D line, which emits light
at 589.3nm wavelength or 5.09E14 Hz. Unfortunately, the available equipment could
not determine dielectric constant at visible light frequency range, 3.75E14 to 7.5E14
Hz. In the studies conducted by Nelson and Trabelsi (2006) and Sacilik et al. (2007) on
organic materials, wheat and safflower seed respectively, concluded that when the
dielectric constant was measured at lower temperature (25°C) and lower moisture
content (5%), the dielectric constant decreased linearly as the frequency increased.
Study on ceramics also showed the linear relationship between dielectric constant
and frequency (Yun et al. 2009). Hence, the RI of fibre film was estimated by fitting
the dielectric constant curve with a linear line and then using the equation to
calculate dielectric constant at 589.3nm wavelength. The former two studies
measured the dielectric constant in higher frequency range compare to 10-10E06 Hz
in this study. Thus, their approaches were more reliable as the dielectric constant
curve obtained here was not straight at the starting point. Table 8 listed the RI of the
fibre films using the linear line approximation.

Table 8 Refractive indices measurements using dielectric constant approach.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>RI at 589.3nm</th>
<th>Sample ID</th>
<th>RI at 589.3nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-10</td>
<td>0.99</td>
<td>B-10</td>
<td>1.26</td>
</tr>
<tr>
<td>A-20</td>
<td>0.93</td>
<td>B-20</td>
<td>1.33</td>
</tr>
<tr>
<td>A-30</td>
<td>0.75</td>
<td>Set C</td>
<td>1.34</td>
</tr>
<tr>
<td>A-40</td>
<td>1.51</td>
<td>Set D</td>
<td>1.02</td>
</tr>
<tr>
<td>A-50</td>
<td>1.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Because the results were estimations, there was no pattern to follow. A-10, A-20 and A-30 samples showed RI less than 1, which was impossible as the light could not travel faster in films than in vacuum. In summary, this was not a dependable approach.

As mentioned in Nogi et al. (2005), when micron-sized filler was used in composites, the refractive indices of filler and matrix must match to the third decimal place to avoid light scattering. The study used 9 resins with different RI ranging from 1.49 to 1.64 to make nanocomposite film with bacterial cellulose films. Because the light transmittance of the nanocomposite peaked when incorporated into the resin with RI of 1.56 to 1.60, the authors assumed the RI of bacterial cellulose film was also in that range. For the nanocomposites produced in this study using B-10 fibre films, the highest light transmittance was found when using Resin 1 as matrix. Although the high light transmittance might attribute to its smaller molecular size, it was safer to say that the RI of B-10 film was closer to 1.53 than using the dielectric constant approach. Brandrup et al. (1999) also found that the RI of cellulose was 1.618 along the fibre axis and 1.544 in the transverse direction.

4.1.7 Thermal Stability

Thermal gravimetric analysis (TGA) and thermal mechanical analysis (TMA) were performed to investigate the thermal degradation and deformation characteristics of nanofibre film derived from wheat straw.

4.1.7.1 Thermal Gravimetric Analysis

Thermal degradation was evaluated by the change of mass verses temperature. The TGA curves of chemically treated wheat straws were represented in Figure 9. The light shaded colors represent their derivative of weight change curves. The mechanically treated wheat straw showed similar single-step curves with different amounts of residue and initial degradation temperatures.
Figure 10 Thermal gravimetric curves of chemically treated wheat straw.

The on-set degradation temperature, $T_{on-set}$, the temperature at maximum weight loss rate, $T_{max}$, and the weight percentage of residue, $W_R$, of all tested samples were listed in Table 10. Results for nanofibre film were the average of the fibre films made from A-30, B-10, B-20, Set C and Set D.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{on-set}$ (°C)</th>
<th>$T_{max}$ (°C)</th>
<th>$W_R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>267</td>
<td>314</td>
<td>24.7</td>
</tr>
<tr>
<td>Alkaline Treated</td>
<td>331</td>
<td>354</td>
<td>11.5</td>
</tr>
<tr>
<td>Bleached</td>
<td>328</td>
<td>360</td>
<td>8.55</td>
</tr>
<tr>
<td>A-30 (Powder)</td>
<td>303</td>
<td>323</td>
<td>25.2</td>
</tr>
<tr>
<td>B-10 (Powder)</td>
<td>315</td>
<td>350</td>
<td>19.3</td>
</tr>
<tr>
<td>B-20 (Powder)</td>
<td>314</td>
<td>349</td>
<td>19.2</td>
</tr>
<tr>
<td>Set C (Powder)</td>
<td>321</td>
<td>352</td>
<td>18.3</td>
</tr>
<tr>
<td>Set D (Powder)</td>
<td>323</td>
<td>357</td>
<td>17.3</td>
</tr>
<tr>
<td>Nanofibre Film</td>
<td>309</td>
<td>339</td>
<td>22.1</td>
</tr>
</tbody>
</table>

The results clearly illustrated that the thermal stability of wheat straw increased after each step of chemical treatment. Since the amorphous hemicellulose and lignin were removed, the degree of crystallinity was also increased resulting in improved thermal stability. The weight of residue had decreased along the chemical treatments.
as ashes and inorganic substances were washed away. The removal of calcium oxalate crystals was another possibility for lowered residue value as described in Alemdar and Sain (2008). Jonoobi et al. (2009) suggested that the presence of lignin would also increase the residue content as it degrades slower.

For the powder-form nanofibres from each set, the on-set degradation temperatures were above 300°C, but the values were less than the bleached wheat straw, which contradicts to the assumption that higher crystallinity would lead to better thermal stability. The reason for this might be that the samples were ethanol exchanged. The less polar ethanol suppressed the hydrogen bonding formation during drying. But the hydrogen bonds might enhance the thermal stability as they reduce the heat transfer rate throughout the samples. The on-set thermal degradation temperature was particularly low for A-30 sample. As discussed previously, Set A contained many larger diameter fibres. These large fibres had lower crystallinity comparing to the finer ones, thus, reducing the overall thermal stability of the sample. The residue value of A-30 was higher comparing to the others because of the inorganic substances that had fallen into the fibre suspension.

Because there was no further chemical reaction after bleaching and there was no addition of new substances into the bleached wheat straw, the residue values of the test samples should stay around the value reported for bleached wheat straw. However, the residue values were about 100% more than the value of bleached wheat straw. Besides the presence of inorganic particle, Set D, which had never been through the defibrillator, also had a 17.3% of residue. This was a very baffling phenomenon as the powder-form samples were only run because the author assumed the high residue value for dried nanofibre film was caused by insufficient heat transfer due to their high density. If ascribe to the inorganic particles, then it could not explain the high residue presented in Set D sample. Also, when Set D was run with air in stead of nitrogen, there was practically nothing left at the end, meaning there were little inorganic substances. At this moment, there was no conclusive reason for the cause of this phenomenon.

Due to the thickness and density differences of fibre films, the degradation
characteristics of them were incomparable. Therefore, an average was reported. The low on-set degradation for fibre films was attributed to the specimen mass. As the TGA pan could only contain a small volume of sample, and in order to represent the sample that would be used in the composite, 5 by 5mm squares with thickness around 50 microns were tested. The samples only weighted around 2mg, while for the powder-formed samples, the specimen mass were 20mg. The reduced on-set degradation temperature was probably due to the fact that small specimens have a larger area to volume ratio. Therefore, it would be attacked more rapidly (Ehrenstein et al. 2004). ISO11358 requires the sample mass to be at least 10mg for the same reason. The high residue content was caused by the high density of fibre films compared to their lose powder ones, which reduces the heat transfer rate.

Alemdar and Sain (2008) reported 296°C for the on-set degradation temperature of nanofibres from wheat straw. A degradation temperature of 351°C was found in the study of Jonoobi et al. (2009) for the nanofibres from kenaf. The high thermal stability could be explained by the high crystallinity of the kenaf nanofibres reported at 81.4% comparing to wheat straw nanofibre at 66.4%.

4.1.7.2 Thermal Mechanical Analysis

Only B-10 film was tested for coefficient of linear thermal expansion (CLTE) as it would be the base for the making of nanocomposite. Figure 11 below was the dimension change verses temperature curve of B-10 film. The average CLTE over the temperature range of 20-120°C was found to be 0.45ppm/K by dividing the slope of the curve by the initial sample length, 13.5mm. Nogi et al. (2009) referenced 0.17ppm/K as the CLTE for cellulose nanofibres from the work by Nishino et al. (2004) on all cellulose composite. Another study conducted by the same group reported 3ppm/K and 8.5ppm/K of CLTE for bacterial cellulose and softwood nanofibres respectively (Nakagaito et al. 2010).

The low CLTE found in this study might be attributed to the moisture content of the specimen. The author tested an oven-dried specimen that was kept in a
dessicator for 2 hours before testing and it showed negative dimension change, i.e., it was shrinking as the temperature went up. The slope of the curve was -1.56μm/K in the same temperature range (20-120°C). That was -11.5ppm/K in terms of CLTE. The moisture regained back to the specimen was considered as the reason. Therefore, the rest of the specimens were kept in an oven at 105°C. However, time had to be spent on mounting the samples to the TMA clamps and the humidity in the equipment room was 54%. Therefore, the samples could of have picked up moisture and the change in expansion might have been cancelled out by the shrinkage to certain extend. If assuming the dimensional change of B-10 film was completely counteracted by the shrinkage, the B-10 nanofibre film would have a CLTE of 12.0ppm/K. The shrinkage of nanofibre film may not impose any effect on the composite samples as acrylate resin do not shrink as temperature goes up and the adhesion between resin and film could prevent the film from shrinking.

\[ y = 0.0611x - 2.1703 \]

\[ R^2 = 0.9607 \]

![Figure 11](image.jpg) Coefficient of linear thermal expansion of B-10 fibre film.

4.1.8 Summary

Fibre dispersion and uniformity in fibre diameter were the key factors that influence the fibre quality. Other factors including degree of polymerization, crystallinity, film thickness, density and surface smoothness were also directly linked
to the fibre film’s tensile, optical and thermal properties. Although Set C possess superior properties in many aspects, the production needed an extra step, which would use more energy and increase the production cost, and the delicacy of the film was a disadvantage. Therefore, after close investigation, films made from B-10 suspension with density of 1.26g/cm$^3$ were chosen as the base for making nanocomposite films with acrylate resins.

4.2 Properties of Cured Acrylate Resins

Acrylate resins were the matrices of the nanocomposites. In order to assess the effectiveness of using nanofibre film as reinforcement filler, the properties of cured acrylate resins were studied as the base reference.

4.2.1 Effect of Photoinitiator Concentration and UV Dosage on Resin Cureness

There are no specifications or a simple test to conduct in order to judge whether a formula is cured. Even though under cure and over cure can lead to unsatisfactory properties, to what extend to cure the formula depends totally on the final applications and desired properties. Many studies based on their formulas on the optimal photoinitiator concentration which depends on many factors, such as cost, UV source and thickness of the coating (Lowe 1997). An increase in photoinitiator concentration can increase the cure rate and the depth of cure by generating more radical species at the beginning. However, once passed the optimal concentration, the rate of reaction will level off and even decrease because of excess radicals formed comparing to the active site. This also causes the reaction to be retarded very rapidly and form shorter chains as the termination reactions become dominant before the initiated species start to propagate (Crivello et al. 1998). Photo-DSC or real-time FTIR are the mostly employed methods to test for carbon carbon double bond conversion (Lee et al. 2003). Normally, the aim is to achieve above 90% of conversion to ensure proper chain growth or crosslinks. Increasing photoinitiator concentration can decrease film strength, increase flexibility, reduce chemical and
mechanical resistance as the chains are shorter. Curing duration also affects the final properties of the resin at the end (Crivello et al. 1998). Longer curing time would allow the active species to react with the adjacent ones and form longer chains.

The effect of using dual photoinitiators of PI1 and PI2 at 1%-0.1% and 2%-0.2% concentrations were studied along with different curing time. The exposure duration varied from 1 to 2 to 3 minutes on each side. The sample denoted as Resin 1 1-0.1-2 represented for Resin 1 cured with 1% of PI1 and 0.1% of PI2 for 2 minutes on each side.

4.2.1.1 Dynamic Mechanical Analysis

The cross-link density or the moles per volume was examined by the dynamic mechanical analysis (DMA) by applying a small oscillating force in tension mode while the temperature ramped up to reach the samples rubbery plateau. Although pure Resin 1 and Resin 3 showed not much difference in tensile properties, Resin 1 was very susceptible to heat. The test specimens rendered around 50-70°C. 55°C was chosen to obtain the storage modulus, $E'$, at the rubbery plateau for Resin 1. The temperature was well above the Tg of Resin 1 at 28°C. $E'$ of Resin 3 samples were taken at 110°C. The crosslink density was calculated by the equation listed in section 3.2.3.1. The DMA graphs, $E$'s and cross-link densities were presented in Figure 12 and Table 10 respectively.

![Graph](a)
**Figure 12** DMA curves of a) Resin 1 and b) Resin 3 cured with different photoinitiator concentrations.

**Table 10** Rubbery plateau tensile modulus and cross-link density of acrylate resins cured with different photoinitiator concentrations and UV dosages.

<table>
<thead>
<tr>
<th>Resin 1</th>
<th>$E'$ (Pa) @ 55 °C</th>
<th>$\nu_a$ (mol/cm$^3$)</th>
<th>Resin 3</th>
<th>$E'$ (Pa) @ 110 °C</th>
<th>$\nu_a$ (mol/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1 1-0.1-1</td>
<td>214</td>
<td>26.1</td>
<td>Resin 3 1-0.1-1</td>
<td>322</td>
<td>33.7</td>
</tr>
<tr>
<td>Resin 1 1-0.1-2</td>
<td>210</td>
<td>25.6</td>
<td>Resin 3 1-0.1-2</td>
<td>306</td>
<td>32.1</td>
</tr>
<tr>
<td>Resin 1 1-0.1-3</td>
<td>209</td>
<td>25.5</td>
<td>Resin 3 1-0.1-3</td>
<td>297</td>
<td>31.1</td>
</tr>
<tr>
<td>Resin 1 2-0.2-1</td>
<td>255</td>
<td>31.1</td>
<td>Resin 3 2-0.2-1</td>
<td>339</td>
<td>35.5</td>
</tr>
<tr>
<td>Resin 1 2-0.2-2</td>
<td>252</td>
<td>30.8</td>
<td>Resin 3 2-0.2-2</td>
<td>326</td>
<td>34.1</td>
</tr>
<tr>
<td>Resin 1 2-0.2-3</td>
<td>251</td>
<td>30.6</td>
<td>Resin 3 2-0.2-3</td>
<td>322</td>
<td>33.7</td>
</tr>
</tbody>
</table>

As predicted, increasing photoinitiator concentration and curing time both led to increase in crosslink density, smaller molecular weights or shorter chains. Resin 1 after curing has higher molecular weight than Resin 3 despite that it had lower molecular weight. This was because Resin 1 was a monofunctional acrylic oligomer. It did not crosslink but polymerized linearly, which means there were less active site in Resin 1 than in oligomers that have the same molecular weight but higher functionality. On the other hand, the low shorter chains in Resin 1 also helped the initiating species to migrate more easily. Therefore, when the initiator concentration was increased, Resin 1 curves and crosslink densities using different photoinitiator concentrations were more separated from each other and most of the propagations
were done in the first 2 minutes. As a mono-functional oligomer, doubling the
photoinitiator concentration did not result in doubling or even increase 50% of the
cross-linking density. This suggested that the doubled photoinitiator concentration
was close or had already been passed its optimal level.

For a di-functional oligomer like Resin 3, the chain growth should go up
exponentially before the optimal concentration is reached. Nevertheless, by
doubling the photoinitiator concentration did not raise the overall crosslink density
as well. Resin 3 samples also cured slower than Resin 1 ones as the longer chain
slowed down the propagation process. The differences in $E'$ for sample cured for 2
and 3 minutes on each side still had a big gap, but the gap was getting smaller.

4.2.1.2 Thermal Aging Analysis

The rate of degradation was found to be proportional to the chain length
(Krongauz and Ling 2009). An isothermal analysis was done with TGA at 300°C for 60
minutes and the TGA curves were listed in Figure 13.

The isothermal aging analysis did not show much variation between each sample.
There was less than 1% in terms of weight loss among all samples. The differences
were less pronounced because of the chosen temperature. The initial on-set
degradation temperatures of these two resins were both around 300°C. The better
observation point could lie around the temperature that showed the maximum
weight loss rate, $T_{max}$. The results did not confirm with the findings from DMA in
terms of chain length rankings. But taken in the fact of sample variations and the
minor change in weight loss, specimens cured with higher photoinitiator
concentration did show a slower degradation rate comparing to the lower ones. In
addition, Resin 3 which had higher cross-link density and shorter chain did show a
slower degradation rate comparing to Resin 1.

Because photoinitiators are the most expensive components in a formula and
there was not much difference in terms of molecular weight among samples being
cured with different concentration, therefore the 1% of PI1 and 0.1% of PI2 was
chosen and the curing time was set at 2 minutes on each side to ensure relatively complete reactions. Nevertheless, in the future, the conversion rate should be determined using either photo-DSC or real time FTIR techniques mentioned above to fine tune the photoinitiator concentration and curing time for best results.

![Graph of Weight (%) vs Time (minute) for different resin types and concentrations.](image)

**Figure 13** Isothermal TGA curves of cured Resin 1 and 3 with different photoinitiator concentrations and curing time.

4.2.2 **Tensile Properties**

Tensile properties of 0.5mm thick acrylate films cured using the formula
described in the previous section (4.2.1) were listed in Table 11. The values in parenthesis were standard deviation with at least 5 specimens. Tensile properties, especially Young’s modulus, of Resin 1 and 3 cured with different photoinitiator concentration and duration did not observe any conclusive data to confirm with the storage modulus pattern found in DMA test. Therefore, those numbers was not reported. The reason was that it was very hard to create large area of cured resin with even thickness despite of using a mold. Because the Mylar® sheets were not rigid, the resin may expand and flow around before it was fully cured. Since the extend of cure depends on the thickness as the UV radiation would eventually be stopped when traveling through the resin layer, the test results would not be reliable if the samples with same thickness were not being analyzed. Test specimens for the other experiments were carefully chosen to maintain same thickness as they did not require large sizes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Strain to Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1</td>
<td>21.2 (1.91)</td>
<td>0.34 (0.06)</td>
<td>44 (5.20)</td>
</tr>
<tr>
<td>Resin 2</td>
<td>13.8 (0.44)</td>
<td>0.06 (0.00)</td>
<td>28 (2.52)</td>
</tr>
<tr>
<td>Resin 3</td>
<td>24.7 (1.07)</td>
<td>0.59 (0.00)</td>
<td>20 (2.14)</td>
</tr>
</tbody>
</table>

### 4.2.3 Regular Light Transmittance and Refractive Index

Regular light transmittances and refractive indices (RI) estimated at 589.3nm wavelength of cured Resin 1, 2 and 3 were presented in Table 12.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Refractive Index</th>
<th>% T at 400nm</th>
<th>% T at 600nm</th>
<th>% T at 800nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1</td>
<td>1.32</td>
<td>88.6</td>
<td>90.2</td>
<td>90.4</td>
</tr>
<tr>
<td>Resin 2</td>
<td>1.26</td>
<td>88.3</td>
<td>91.8</td>
<td>92.6</td>
</tr>
<tr>
<td>Resin 3</td>
<td>1.20</td>
<td>91.3</td>
<td>92.3</td>
<td>92.4</td>
</tr>
</tbody>
</table>

Again, the RI measured here was an approximation. In order to prevent light scattering caused by RI mismatch, a better technique or method have to be found to
test RI accurately.

4.2.4 Thermal Properties

4.2.4.1 Glass Transitional Temperature

The glass transitional temperature (Tg) was found by differential scanning calorimeter (DSC). In this study Tg was not only a characteristic property, knowing it also helped to locate the rubbery plateau for the DMA test. Figure 14 showed the 2nd run DSC curves for each resin and the midpoint Tg was shown besides the legend. The Tg of Resin 3 was less profound, but it matched the Tg from the thermal mechanical analysis curve.

![Figure 14 Glass transitional temperatures of Resin 1, 2 and 3.](image)

4.2.4.2 Thermal Stability

The TGA curves of cured Resin 1, 2 and 3 were represented in Figure 15. The light colored ones were the derivative of weight change curve for each resin.

Steps in TGA curves means the materials have different components. All three resins showed a two-step weight loss curve. Resin 2 and 3 are polyurethane acrylates which were made by reacting isocyanate with polyols. The two steps could represent
the disappearance of these two substances from the backbone. The steps were not obvious for Resin 1, but were distinguishable in the derivative curve. There was a little hump at the beginning of Resin 1’s derivative curve as well indicating the disappearance of another substance. Resin 1 was only known as acrylic oligomers. Therefore, the three weight loss steps could be corresponded to the functional groups on the acrylate backbone. The $T_{\text{on-set}}$, $T_{\text{max}}$ and $W_R$ were listed in Table 13. $T_{\text{on-set}}$ of Resin 1 was reported only on the 1st step.

![Thermal gravimetric curves of cured Resin 1, 2 and 3.](image)

**Figure 15** Thermal gravimetric curves of cured Resin 1, 2 and 3.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{\text{on-set}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$W_R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1</td>
<td>364</td>
<td>386</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>424</td>
<td></td>
</tr>
<tr>
<td>Resin 2</td>
<td>312</td>
<td>344</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>446</td>
<td>1.46</td>
</tr>
<tr>
<td>Resin 3</td>
<td>297</td>
<td>335</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>393</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{\text{on-set}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$W_R$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1</td>
<td>364</td>
<td>386</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>424</td>
<td></td>
</tr>
<tr>
<td>Resin 2</td>
<td>312</td>
<td>344</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>446</td>
<td>1.46</td>
</tr>
<tr>
<td>Resin 3</td>
<td>297</td>
<td>335</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>393</td>
<td></td>
</tr>
</tbody>
</table>

4.2.4.3 Coefficient of Linear Thermal Expansion

Coefficients of linear thermal expansion (CLTE) of cured Resin 1 and 3 were
calculated from the dimension change verses temperature curves in Figure 16. Resin 1 did not survive throughout the whole experiment. It broke around 75°C just as in the DMA test. Therefore, the average CLTE of Resin 1 was reported in the 20-75°C range. It was found to be 49.5ppm/K by dividing the slope, 6.66, by the sample length, 13.5mm. The average CLTE of Resin 3 over the 20-120°C range was found to be 35.9ppm/K by dividing 4.84 with 13.5mm as original sample length.

\[
y = 6.6577x - 141.46 \\
R^2 = 0.9927
\]

\[
y = 4.8377x + 28.773 \\
R^2 = 0.8451
\]

Figure 16 Coefficient of linear thermal expansion of cured Resin 1 and Resin 3 sheets.

4.2.5 Summary

A better way to measure RI remained as an issue. After analyzing the cross-link densities of cured resin with different photoinitiator concentrations and curing durations, the resins were decided to cure with 1% of PI1 and 0.1% of PI2 for 2 minutes on each side.

4.3 Evaluation on Nanofibre Reinforced Nanocomposite Films

The serviceability of the nanocomposite films as potential substrates for flexible flat panel screen was investigated and evaluated in this section.
4.3.1 Tensile Properties with Different Percentage of Fibre Loading

Table 14 Tensile properties of Resin 1 and Resin 3 nanocomposites at different fibre loadings.

<table>
<thead>
<tr>
<th>Fibre Loading</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Strain to Failure (%)</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Strain to Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.4%</td>
<td>36.9 (6.38)</td>
<td>2.30 (0.26)</td>
<td>2.73 (0.29)</td>
<td>23.0%</td>
<td>43.5 (8.11)</td>
<td>2.57 (0.52)</td>
</tr>
<tr>
<td>30.4%</td>
<td>55.3 (8.21)</td>
<td>4.02 (0.43)</td>
<td>2.68 (0.14)</td>
<td>33.0%</td>
<td>66.5 (5.40)</td>
<td>3.66 (0.42)</td>
</tr>
<tr>
<td>53.8%</td>
<td>133 (17.5)</td>
<td>7.86 (0.68)</td>
<td>2.59 (0.11)</td>
<td>43.0%</td>
<td>91.2 (12.1)</td>
<td>5.09 (0.89)</td>
</tr>
<tr>
<td>65.8%</td>
<td>161 (16.7)</td>
<td>8.93 (0.67)</td>
<td>2.51 (0.36)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mechanical properties of composites made with Resin 1 and Resin 3 with different B-10 fibre loading in weight percentage were assessed and listed in Table 14. The fibre loading was based on the average of 5 specimens. Higher fibre loading was hard to achieve for Resin 3 composites as the resin was very viscous before curing.

Increase in fibre loading lead to improved tensile strength and Young’s Modulus as fibre films had these qualities compare to the neat resin. To inspect the effect of fibre loading on the final qualities of the composite, the tensile strength and Young’s modulus were plotted against the fibre loading percentage in Figure 17. The blue and red lines represented the values of Resin 1 and Resin 3 composites predicted by the rule of mixtures.
Figure 17 a) Tensile strength and b) Young’s modulus of Resin 1 and Resin 3 composites as a function of fibre loading percentage (blue and red lines represent the value predicted by the rule of mixtures).

For both Resin 1 and Resin 3 composites at lower fibre loadings, the tensile strength and Young’s modulus fell below the lines. Once the fibre loading increased to around 40%, they surpassed the lines. The reinforcing ability of fibre film was based on resin penetration and interfacial adherence. For composite with higher fibre loading, more force was used to scrape the excess resin. Therefore, there would be more resin penetration and the fibre network would hold resin and the tensile properties would be improved. Lower fibre film density may motivate better reinforcing quality for the same reason. This also explained the lower strain to failure. Resin 1 composite showed lower strain to failure may have suggested that Resin 1 adhered to the fibre film better than Resin 3 as Resin 1 has lower viscosity and molecular weight.

Nakagaito and Yano (2008) found the same trend for Young’s modulus of their nanocomposites made with softwood pulp and phenol formaldehyde resin. The tensile strength was not analyzed in their study as they suggested that the data was too scattered to be reliable. In their other study, softwood pulp nanofibre sheet had tensile strength and Young’s modulus of 223MPa and 13GPa respectively. After coating the film with 15-40% of resin, the properties went down to 216MPa and 13GPa (Nakagaito et al. 2010). The results implied that the tensile properties were
also higher than the rule of mixtures had predicted.

### 4.3.2 Regular Light Transmittance

Regular light transmittance scans of Resin 1/3 and B-10 fibre film composites with different fibre loading were presented in Figure 18 along with the scans of neat resins for comparison. The percentage of light transmittance of these composites at 400, 600 and 800nm wavelength were listed in Table 15, as well as the composites prepared with Set C fibre films and B-10 fibre films dried with filtration membrane (B-10M).

![Regular light transmittance over visible wavelength of Resin 1 and Resin 3 composite with different fibre loadings.](image)

Nanocomposites with higher fibre loadings experienced higher transparency because the overall thickness has been reduced. If the composites were corrected with thickness using Beer’s Law, then higher fibre loading would result in lowering the transparency as stated in Nogi et al. (2006). By increasing the fibre content from 23.1% to 65.8% in Resin 1 composites, the percent of regular transmittance increased from 71.0 to 75.9% at 600nm wavelength while the thickness has reduced from 0.17 to 0.06mm. Likewise, the percentage of regular transmittance of Resin 3 composites...
increased from 71.6 to 72.5% by 12% of more fibre loading and the thickness decreased from 0.14 to 0.10mm. Because that neat Resin 3 initially had better transmittance comparing to Resin 1 yet the composites had defeated by their counterparts, it confirmed that resin with smaller molecular weight at the beginning would benefit the composite more as their small molecules can penetrate into the fibre network better, thus having more smoothing effect and reduce surface light scattering.

Despite the fact that B-10M fibre films had high regular transmittance themselves, because the density was slight higher and the surface was smoother, they actually did not create more transparent nanocomposites at the end. Similarly, Set C films can transmit 30.1% of light at 600nm wavelength when the film weighted 0.3g, but once the weight increased to 0.4g, so did the thickness. Therefore, the light had to travel through more length thus reduce the transparency. For detailed discussion on how surface properties and density affects the light transmittance please refer to section 4.1.6.1 for detail.

**Table 15** Percentage of regular light transmittance of fibre films and nanocomposites at different fibre loadings at 400, 600 and 800nm wavelength.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fibre Loading or Density</th>
<th>% T at 400nm</th>
<th>% T at 600nm</th>
<th>% T at 800nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-10</td>
<td>1.26g/cm³</td>
<td>12.2</td>
<td>18.7</td>
<td>24.2</td>
</tr>
<tr>
<td>B-10M</td>
<td>1.38g/cm³</td>
<td>25.9</td>
<td>41.3</td>
<td>52.7</td>
</tr>
<tr>
<td>Set C</td>
<td>1.29 g/cm³</td>
<td>9.33</td>
<td>14.8</td>
<td>18.3</td>
</tr>
<tr>
<td>Neat Resin 1</td>
<td>0%</td>
<td>88.6</td>
<td>90.2</td>
<td>90.4</td>
</tr>
<tr>
<td>Resin 1 B-10</td>
<td>23.1%</td>
<td>54.6</td>
<td>71.0</td>
<td>77.8</td>
</tr>
<tr>
<td></td>
<td>44.1%</td>
<td>60.5</td>
<td>73.8</td>
<td>79.2</td>
</tr>
<tr>
<td></td>
<td>65.8%</td>
<td>62.6</td>
<td>75.9</td>
<td>81.4</td>
</tr>
<tr>
<td>Resin 1 B-10M</td>
<td>23.2%</td>
<td>53.3</td>
<td>69.3</td>
<td>76.3</td>
</tr>
<tr>
<td>Resin 1 Set C</td>
<td>33.9</td>
<td>51.8</td>
<td>66.8</td>
<td>72.7</td>
</tr>
<tr>
<td>Neat Resin 3</td>
<td>0%</td>
<td>91.3</td>
<td>92.3</td>
<td>92.4</td>
</tr>
<tr>
<td>Resin 3 Composite</td>
<td>24.4%</td>
<td>57.8</td>
<td>71.6</td>
<td>77.7</td>
</tr>
<tr>
<td></td>
<td>35.9%</td>
<td>58.5</td>
<td>72.5</td>
<td>78.3</td>
</tr>
<tr>
<td>Resin 3 B-10M</td>
<td>28.4%</td>
<td>54.6</td>
<td>70.5</td>
<td>77.8</td>
</tr>
<tr>
<td>Resin 3 Set C</td>
<td>25.6%</td>
<td>54.9</td>
<td>70.0</td>
<td>75.7</td>
</tr>
</tbody>
</table>
Total light transmittance is the sum of regular light transmittance and diffused transmittance which is caused by internal scattering centers, such as scratches, bubbles, suspended particles. Haze equals to the diffused transmittance divided by the total light transmittance (HunterLab 2008b). As described in MacDonald (2004), haze should be less than 0.7% for polymer based flexible display substrates while the total light transmittance should be higher than 85% over 400-800nm wavelength range. Therefore, in order to meet both criteria, the nanocomposite films need to have a minimum regular light transmittance of 84.4%.

As discussed previously, fibre size, fibre diameter uniformity and presence of out-of-plane fibres in the film were the factors that could affect the regular light transmittance of fibre films and thus of the nanocomposites. Out-of-plane fibres could be reduced by slowing down the filtration process when making fibre films, but their presence was also heavily depend on the fibre sizes and dispersion. Hence, how the fibre suspensions were produced was the key to improve composites transparency. By lowering the density of the fibre film is another way to enhance overall transparency but it is always associated with compromised strength. Furthermore, reducing the fibre film thickness can also make the composites transmitting more light, but may create handling problems due to the delicacy of thin films. Likewise, reducing the overall composite thickness could also improve the transparency. However, according to the results obtained, it would not have a dramatic effect. Lastly, by accurately matching the RI of fibre films and resins, the transparency could also be improved.

Another problem was to obtain total light transmittance above 85% throughout the visible wavelength range since cellulose transmits less light at lower wavelength. Even though Nakagaito et al. (2010) had obtained 85% of regular light transmittance for nanocomposites made with softwood and even 95% with bacterial cellulose at 800nm wavelength, the lower end was always below the bar and wer in the 60-80% range.
4.3.3 Degradation Temperature and Coefficient of Linear Thermal Expansion

TGA curves of Resin 1 and Resin 3 nanocomposites with 30% fibre loading were listed in Figure 19 along with curves of cured resin and B-10 fibre film for comparison.

![TGA curves of Resin 1 and Resin 3 nanocomposites.](image)

**Figure 19** Thermal degradation curves of a) Resin 1 and b) Resin 3 nanocomposites.

By covering the nanofibre film with a more heat resistant layer of resin, the initial degradation temperature was assumed to be delayed as the heat could only...
attack the fibre film from the sides and the heat penetration would be slowed down by the resin cover. However, from the TGA curves, the two components in the composite acted like if they were sitting next to each other. The addition of another component did change the shape of the curves.

The two-step weight loss was not very obvious for pure Resin 1, but the two derivative peaks after 350°C were distinctive. By adding the nanofibre film, the latter step became more visible. The minor weight loss at the temperature range 150-250°C led to a decrease in $T_{\text{on-set}}$ to 304°C comparing with B-10 film at 311°C, this also moved up the $T_{\text{max}}$ of the composite from B-10’s 335°C to 329°C. The two derivative peaks remained the same for the composite comparing to pure resin indicating the fibre degradation was at its steady state that did not interfere with the resin. The 30% addition of fibre only changed the weight residue $W_R$ of pure Resin 1 from 4.70% to 7.96%. Since the $W_R$ of B-10 film was 22.0%, a 30% of fibre loading would have a $W_R$ of 9.88%. Heat might be built up inside the composite as the resin could not dissipate the extra heat easily. In addition, when the resin decomposes, it releases carbon dioxide and forms alcohols which might degrade the nanofibre further resulting in less residues at the end (Krongauz et al. 2009).

Similar observation was found with Resin 3 composite. The initial $T_{\text{on-set}}$ of the B-10 film was reduced from 311°C to 299°C by the addition of Resin 3 because Resin 3 starts to degrade earlier at 297°C. The 2nd step of the composite weight loss curve was delayed comparing to pure resin due to the rate of degradation slowed down for the fibre film. The residue again was lower than if calculated by weight percentage of each component in the composite. It would be attributed to the same reason described above.

The coefficient of linear thermal expansion (CLTE) of Resin 1 and Resin 3 composites with 28% and 30% of fibre loading respectively was found by dimensional changer verses temperature curve showed in Figure 20.

With the initial sample length of 13.52 and 13.50mm, the CLTE of Resin 1 and Resin 3 were calculated to be 8.53 and 9.80ppm/K respectively. As the curves have shown, the fibre film successfully suppressed the deformation caused by raising
temperature. The formerly distinctive characteristics of pure Resin 3 undergone the glass transition stage was almost faded away. However, because Resin 3 originally had lower CLTE than Resin 1 and the fibre loading in Resin 3 was slightly higher suggested that the interfacial adhesion with fibre film was not as good as Resin 1. This also confirmed with findings from their tensile properties.

Higher fibre loading would further reduce the CLTE of the composites as stated in Nogi et al. (2006). It mentioned that with only 7.4% of bacterial cellulose loading, the CLTE could reduce from 86ppm/K to 38ppm/K. By coating the fibre film thinly which increased the fibre loading content to 30.4%, the CLTE was further reduced to 15ppm/K. Nakagaito et al. (2010) also obtained 13ppm/K of CLTE with 60-85% of loading with softwood derived nanofibres.

![Graph showing the relationship between temperature and dimension change for Resin 1 and Resin 3 composites.](image)

**Figure 20** Coefficient of linear thermal expansion of B-10 fibre film reinforced nanocomposites.

Overall, the composite exhibited good heat resistance that Resin 1 and Resin 3 composites both had initial degradation temperature around 300°C and CLTE less than the minimum requirement of 20ppm/K. With higher fibre loading, the TGA curves of the composite might change slightly, as well as the residue value, but it should not change the thermal stability of the composite as both the resin and the fibre film had high degradation temperature. Higher fibre loading would also lower the CLTE.
4.3.4  Bending Property

4.3.4.1  Visual Comparison

Pictures of Resin 1 and Resin 3 nanocomposite with 40% and 29% of fibre loading respectively were shown in Figure 21. The dotted blue lines were the center axes of the composites when subjected to bending.

Resin 1 Before  
[Image of Resin 1 Before]

Resin 1 After  
[Image of Resin 1 After]

Resin 3 Before  
[Image of Resin 3 Before]

Resin 3 After  
[Image of Resin 3 After]

Figure 21 Visual comparison of Resin 1 and Resin 3 nanocomposites before and after bending test.

No visual observation suggested that there was any white-zone caused by stress. The bottom of Resin 3 composite was damaged because of mishandling rather than damage caused by bending.
4.3.4.2 Tensile Properties

The tensile strength and Young’s modulus of the Resin 1 and Resin 3 composites after aging were 99.95MPa and 5.99GPa, and 49.96MPa and 2.82GPa respectively. The numbers fell nicely between the results with higher and lower fibre loading obtained from Table 14. In addition, the failure of the test specimens did not occur at the center axis of the folding action. Rather, the specimens broke at point where the thickness was the highest (could be the center axis) as the fibre loading was lower at that point. Therefore, there was no or little damage caused by folding the composites back and forth for 1000 times.

4.3.4.3 Light Transmittance

*Table 16* listed the percentage of regular light transmittance of the specimens before and after repetitive folding action at different wavelength.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>% T at 400nm</th>
<th>% T at 600nm</th>
<th>% T at 800nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1 B-10</td>
<td>Before</td>
<td>59.1</td>
<td>73.6</td>
<td>79.1</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>58.2</td>
<td>72.4</td>
<td>78.0</td>
</tr>
<tr>
<td>Resin 3 B-10</td>
<td>Before</td>
<td>58.5</td>
<td>72.1</td>
<td>78.2</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>58.3</td>
<td>72.0</td>
<td>78.1</td>
</tr>
</tbody>
</table>

About 1% of light transmittance was lost after bending the Resin 1 nanocomposite while Resin 3 composites did not experience any decrease in transparency. The 1% loss in Resin 1 composites was mostly caused by surface wear and tear against the copper tube during the test. Resin 3 was rated by the manufacturer to have excellent abrasion resistance. This was probably why there was no reduction in light transmittance. The abrasion resistance of the composites would be compared with the abrasion test.

Overall, by bending the nanocomposites over an 1-inch diameter radius for 1000 times did not exposit effects that renders the serviceability of the composites.
4.3.5 Abrasion Resistance

Nanocomposites made with Resin 1 and Resin 3 with 64 and 35% of fibre loading were tested for abrasion resistance with 100 abrasion cycles according to ASTM D1044. The abrasion wheel hit the samples 3cm away from the center and with 1cm width. Visual comparison of the nanocomposites after abrasion cycles were represented in Figure 22.

Resin 1 composite clearly showed a hazy ring at where the abrasion wheel had contacted. Resin 3 composite also had a hazy ring but it was very unnoticeable. The specimens were then tested for regular transmittance to check the reduction in transparency around the abraded area.

![Resin 1 and Resin 3](image)

**Figure 22** Visual comparisons of Resin 1 and Resin 3 with 100 abrasion cycles.

As shown in Table 18, Resin 1 composites had around 30% reduction in regular light transmittance, while Resin 3 showed merely 2% decrease. From visual observation, the low fibre loading Resin 1 sample did not expose the fibre film after the test. Therefore, the abrasion only did damage on the resin coating rather than worn through the coating, which could also reduce the transparency. Overall, despite of the viscous nature of Resin 3, it has showed excellent abrasion resistance after curing that makes it more suitable for daily uses.
Table 17 Percentage of regular light transmittances of Resin 1 and Resin 3 after 100 abrasion cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>% T at 400nm</th>
<th>% T at 600nm</th>
<th>% T at 800nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1 B-10</td>
<td>Before</td>
<td>62.6</td>
<td>75.8</td>
<td>81.2</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>31.5</td>
<td>43.4</td>
<td>51.5</td>
</tr>
<tr>
<td>Resin 3 B-10</td>
<td>Before</td>
<td>58.4</td>
<td>72.4</td>
<td>78.3</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>55.8</td>
<td>70.1</td>
<td>76.5</td>
</tr>
</tbody>
</table>

4.3.6 Effect of Thermal Aging

4.3.6.1 Discoloration

The discoloration of aged composite was not noticeable with naked eyes. By using a spectrophotometer, the CIELAB color space coordinates of the background, and the composite before and after aging was found and listed in Table 18.

Table 18 CIELAB color space coordinates of nanocomposites before and after aging.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Condition</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td></td>
<td>120</td>
<td>7.71</td>
<td>3.50</td>
</tr>
<tr>
<td>Resin 1</td>
<td>Before</td>
<td>113</td>
<td>7.97</td>
<td>7.46</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>113</td>
<td>8.08</td>
<td>8.25</td>
</tr>
<tr>
<td>Resin 3</td>
<td>Before</td>
<td>113</td>
<td>7.97</td>
<td>7.39</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>113</td>
<td>8.03</td>
<td>7.96</td>
</tr>
</tbody>
</table>

The L* coordinate has a limit between 0-100, but the spectrophotometer always reads numbers higher than 100 even with the white calibration background. The L* coordinate measures the lightness of a sample was reduced by layering a piece of composite on top. However, the lightness did not change for the unaged and aged sample indicating minor discoloration. The positive a* coordinates represent redness. There was relatively little change, less than 0.1 of a point, for samples before and after aging. On the other hand, the positive b* coordinates indicating yellowness changed 0.6-0.8 of a point. Because Photoshop only take integers and the b* coordinates changed almost from 7 to 8 while the a* stayed relatively same for samples before and after aging, two color swatches of CIELAB coordinates, 90-8-7 and 90-8-8 were generated (Figure 23). The lightness was reduced to 90 and a* was
not changed to 0 for a more visible comparison.

**Figure 23** Color swatches of CIELAB 90-8-7 and 90-8-8 for unaged and aged nanocomposites.

The pinkness could be ignored as it was embedded with the calibration background. The samples changed more towards the color yellow when aged, but the magnitude was smaller than represented in the swatches since they did not change for a whole point. Relatively, there was little discoloration after aging and Resin 1 became yellower than Resin 3 due to its longer chain length which made it more susceptible for prolonged heat exposure.

4.3.6.2 Tensile Properties

Tensile strength and Young’s of Resin 1 composite with 53.6% of fibre loading after aging was 135MPa and 7.89GPa. Comparing with 133MPa and 7.86GPa at a fibre loading of 53.8% before aging, there was no adverse effect. For Resin 3 composite with 37.6% of fibre loading after aging, the properties were 81.1MPa and 4.11GPa which fell nicely between the values from Table 14. Therefore, aging at 70°C for 7 days did not reduce the tensile properties of the composites. The results also suggested that there was no post-curing at this temperature.

4.3.6.3 Light Transmittance

Percentage of regular light transmittance of Resin 1 and Resin 3 nanocomposites before and after thermal aging was listed in Table 19 and had shown no adverse effect caused by aging.
Table 19 Percentage of regular light transmittance of Resin 1 and Resin 3 nanocomposites before and after aging.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>% T at 400nm</th>
<th>% T at 600nm</th>
<th>% T at 800nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1 B-10</td>
<td>Before</td>
<td>58.4</td>
<td>73.2</td>
<td>79.5</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>58.3</td>
<td>73.4</td>
<td>79.4</td>
</tr>
<tr>
<td>Resin 3 B-10</td>
<td>Before</td>
<td>58.7</td>
<td>72.7</td>
<td>78.3</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>58.8</td>
<td>72.9</td>
<td>78.5</td>
</tr>
</tbody>
</table>

In conclusion, aging at 70°C for 7 days caused minor discoloration but kept the integrity of the composites’ tensile and optical properties.

4.3.7 Summary

To summarize, nanocomposites made with B-10 fibre film and Resin 1 or Resin 3 resin showed excellent tensile properties and flexibility. According to MacDonald (2004) and Choi et al. (2008), the nanocomposites also met the minimal requirement for thermal stability and CLTE as shown in Table 20. However, the light transmittance was still below the standard. Improving the fibre film quality and matching the refractive indices of fibre film and resin were the keys to ensure high transparency of composites. Resin 3 showed superior abrasion resistance comparing to Resin 1. By solving the transparency issue, and testing the composites for barrier properties, chemical resistance and surface roughness and meeting the minimum requirements would then guarantee that the composites are suitable for making the substrate of a flexible flat panel display.

Table 20 Comparison of properties of nanocomposite films made in this study and minimal requirements for polymer based flexible display substrates.

<table>
<thead>
<tr>
<th>Results</th>
<th>Minimal Requirements</th>
<th>Verdicts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1: 65.8-81.4% (regular transmittance)</td>
<td>Total light transmittance over visible wavelength range &gt;85%</td>
<td>Fail</td>
</tr>
<tr>
<td>Resin 3: 58.5-78.3% (regular transmittance)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resin 1: 304°C</td>
<td>Degradation temperature &gt;150°C</td>
<td>Pass</td>
</tr>
<tr>
<td>Resin 3: 299°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resin 1: 8.53ppm/K</td>
<td>Coefficient of linear thermal expansion (CLTE) &lt;20ppm/K</td>
<td>Pass</td>
</tr>
<tr>
<td>Resin 3: 9.80ppm/K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Able to bend over 1 inch diameter radius 1000 times without jeopardizing tensile properties, transparency and appearance</td>
<td>Able to bend over 1 inch diameter radius 1000 times</td>
<td>Pass</td>
</tr>
</tbody>
</table>
Chapter 5  Conclusion Remarks

5.1 Summary of Findings

Nanofibres, which possess unique physical and chemical properties, can be readily produced using established methods described in Alemdar and Sain (2008), Jonoobi et al. (2009), Abe and Yano (2009) and Henriksson et al. (2008). However, their proven excellent mechanical strength achieved little success as reinforcing filler using the conventional composite manufacturing process because of the abundant hydrogen bonding sites at the fibre surface. On the other hand, lamination or impregnation of dried nanofibre film with optical polymers had stood out to have low coefficient of linear thermal expansion (CLTE) and good mechanical properties without decreasing the transparency too much. In this study, nanocomposite film was successfully prepared with nanofibres derived from wheat straw and polyurethane acrylate resins using UV radiation induced curing.

Nanofibre suspension was successfully made according to the method described in Alemdar and Sain (2008) with minor modifications. The yield of bleached wheat straw pulp, 35%, was assumed to be the yield of nanofibres as there was little loss during transfers throughout the defibrillation process. The yield of paper grade bleached kraft pulp is usually around 45-50%, but the tensile strength is much lower comparing to the nanofibres because of their size (Smook 1994). A calculation is done to determine the weight of softwood needed to generate the same strength as the wheat straw nanofibres. Specific strength of softwood kraft pulp was reported to be 52N·m/g at the Pulp and Paper Center, University of Toronto. Specific strength is calculated by dividing the maximum tensile strength by the density of the specimen. Therefore, the specific strength of B-10 fibre film specimen with 181MPa of strength and 1.27g/cm$^3$ of density was calculated to be 143N·m/g. Assuming the density of the softwood specimen is the same as B-10 fibre film and takes the yield into account, then approximately 2 times more raw material (softwood) is needed to produce
specimens that have the same strength as the B-10 films. Thus, by using wheat straw, an agriculture residue, and add one step of mechanical treatment, half of the wood source can be saved to achieve the same tensile results. This fact adds environmental values to the nanofibres created in this study.

Nanofibre dispersion and uniformity in nanofibre diameter were the key factors that influence the nanofibre quality and thus the final composite quality. Other factors including degree of polymerization, crystallinity, film thickness, density and surface smoothness were also directly linked to the fibre film’s tensile, optical and thermal properties. After close investigation, films made from B-10 suspension with density of 1.26g/cm$^3$ were chosen as the base for making nanocomposite films with acrylate resins.

Because photoinitiators are the most expensive components in a formula and there was not much difference in terms of molecular weight among samples being cured with different concentration, therefore 1% of PI1 and 0.1% of PI2 was chosen to cure the two types of acrylate resins, Resin 1 and Resin 3, and the curing time was set at 2 minutes on each side to ensure relatively complete reactions.

Nanocomposite films thus made showed excellent tensile properties and flexibility. Resin 3 had superior abrasion resistance that was ideal for portable devices. According to MacDonald (2004) and Choi et al. (2008), the nanocomposite film also met the minimal requirement for thermal stability and CLTE. However, the light transmittance was still below the standard. Improving the fibre film quality matching the refractive indices of fibre film and resin were the keys to ensure high transparency of composites.

5.2 Future Work and Recommendations

Fibre strength, thermal stability and light transmittance would benefit from improved fibre dispersion and diameter uniformity. Uniformity in fibre diameter is especially important in ensuring high transparency of the final nanocomposite films. Therefore, the nanofibre production process has to be fine tuned to ensure these
qualities.

SEM images of nanofibre sheets may be employed as a better technique to observe the fibre morphology and ensure that the fibre diameters are in a narrower range. These images can examine larger quantity of fibres at once that provide a more representative view of the nanofibre morphology comparing to TEM images that are more subjective in terms of the shot location.

In addition, better refractive index measurement is needed to make sure that the light transmittance of nanocomposites is not jeopardized by differences in RIs of the materials; despite of Nogi et al. (2005) found that cellulose nanocomposite was not highly dependent on RI matching.

Total light transmittance and haze needs to be measured to ensure optical transparency.

Clear acrylates with different physical properties, such as mechanical strength, hardness and glass transition temperature, may be used to investigate their influences on the final composite properties. A more robust nanocomposite film can be produced with acrylates resin that cures rigid.

The surface properties of the resin used should be analyzed to check if the surface is compatible with the other components in a display system. For example, the surface tension of the composite when matches the 1st printing layer of an OLED system can avoid addition of surfactants.

The determination of acrylate double bond (C=C) conversion rate is suggested by using either photo-DSC or real time FTIR techniques to optimize the photoinitiator concentration and curing time for best results and economic purposes.

As discussed in the literature review section (2.3), the barrier properties of the nanocomposites are also important for making substrates of display systems. In this study, the film was casted inside the acrylate resin and cured. After curing, the edges of the film were covered by the excess resin. Because nanofibres are hygroscopic, the excess resin acts like a barrier to prevent moisture absorption. If the composites are cut along the edges, the fibre component would be exposed allowing moisture to penetrate, thus affect the composite quality. One of the main goals to use nanofibre
reinforced polymer as display substrates is to free the conventional batch process with glasses to a more productive roll-to-roll process. Therefore, the nanofibre films need to be cut into the desired shapes before the actual curing to avoid exposing them in the actual product as the uncured resin would flow around the incisions and block up the exposed areas. Alternatively, the composites could be sealed at the end using desired sealants.

By solving the transparency issue, and testing the composites for barrier properties, chemical resistance and surface roughness and meeting the minimum requirements suggested in MacDonald (2004) and Choi et al. (2008) would then guarantee that the composites are suitable for making the substrate of a flexible flat panel display.
Chapter 6  References


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