Preparation and Characterization of Cellulose-Silica Nanocomposites

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Preparation and Characteristics of Cellulose/Silica Nanocomposites

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A dissertation submitted in partial fulfillment of the Final Year Project 2 (STF 3015) course

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DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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List of Abbreviations

EDX       Energy Dispersive X-ray
FTIR      Fourier Transform Infrared
HCl       Hydrochloric Acid
HNO₃      Nitric Acid
H₂O       Water
H₂SO₄      Sulfuric Acid
H₃PO₄      Phosphoric Acid
KBr       Potassium Bromide
NaOH      Sodium Hydroxide
SEM       Scanning Electron Microscope
SiO₂       Silicon Dioxide
TEM       Transmission Electron Microscope
TEOS      Tetraethoxysilane
UV/Vis    Ultraviolet/Visible
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Preparation and Characterization of Cellulose-Silica Nanocomposite

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ABSTRACT

Environmental concerns of waste paper have led a demanding push to manage the increasing waste paper from daily use. Recycling paper has not been effective in improving the quality of paper. To address this problem, cellulosic waste materials were converted into useful nanocomposite. This provides a very cost-effective way to reduce landfill wastes. NaOH/thiourea/urea solvent was used to dissolve cellulose under suitable conditions as it is environmentally friendly and cheap. Silica sol was prepared using sol-gel method and added to dissolved cellulose to prepare cellulose nanocomposite. The morphology and changes in functional groups were characterized using Scanning Electron Microscope (SEM) and Fourier Transfer Infrared (FTIR) spectroscopy.

Keywords: Silica nanoparticles, Nanoprecipitation, Sol-gel technique, Nanocomposite

ABSTRAK


Kata kunci: Nanopartikel silica, nanoprecipitation kaedah sol-gel, nanokomposit
1.0 INTRODUCTION

The amount of waste paper produced and consumed annually in a global scale has exceeded one million tons (Uyigue & Okwonna, 2013). In the study, they also mentioned that despite recycling being proposed and successfully applied in daily life, the results weren’t satisfactory due to the lower grade paper produced after recycling. This is because of the reduction in length of the fiber.

With its advantages such as high mechanical strength, rigidity, chemical stability, and biodegradability (Heinze & Liebert, 2001), cellulose can be utilized to produce components in the automotive industries (Bajpai & Singh, 2013). It has also been acknowledged as one of the most abundant and reliably renewable resource, and as a potential alternative to petroleum products (Ma, Zhou, Li, Li, & Ou, 2011). Although the sources of cellulose are unlimited, the major concern here is the expense needed for the production and proper waste management of cellulose (Uyigue and Okwonna, 2013). The use of a green technology would possibly lead to reduced waste in simultaneous to reduced cost of paper production in the long run.

Nanoparticles, on the other hand, have unique properties that are influenced by size, shape and dispersion stability (Rao, Muller, & Cheetham, 2004). Combining both properties, composites of cellulose reinforced with nanoparticles can possibly synthesize an enhanced substance with synergic properties of both components (Sinha Ray & Okamoto, 2003). Nevertheless, the advance is a case-to-case basis, depending on multiple factors such as aspect ratio, dispersion extent and interactions between the polymer matrix and the nanofiller (Fukushima, Tabuani, & Camino, 2009).
Their use and desirable properties draw in huge attention as a successfully synthesized nanocomposite can bring to the production of new substances of desired properties without disrupting the balance of the ecosystem and also help to decrease the amount of waste generated. This is consistent with Dhakal, Zhang, and Bennett (2012) findings that natural fiber reinforced polymer composite has been currently favored for its convenience without disrupting the balance of the ecosystem. It is also foreseen as a replacement for petrochemical based substances (Banerjee et al., 2013).

By adding silica, the nanocomposites will have an added value of effective superhydrophobic property (Pinto, Marques, Barros-Timmons, Trindade, & Neto, 2008), which is applicable in self-cleaning, anti-adhesive coating (Gonçalves, Marques, Trindade, Neto, & Gandini, 2008), contamination prevention (Shang et al., 2004) and corrosion (Roach, Shirtcliffe, & Newton, 2007), and distilling and microfiltering processes (Zhou, Shi, & Jin, 2014).

In this study, cellulose was extracted from ground shredded waste paper by chemical treatment. Moderate pretreatment method was chosen as the paper contained minimal ink particles, and lignin and hemicelluloses residues. The pretreated sample was dissolved in NaOH/thiourea/urea solution and mix with silica to form cellulose-silica nanocomposite.
1.1 Research Question

- How does the properties of synthesized cellulose-silica nanocomposite change by using cellulose fiber and cellulose nanoparticles?

1.2 Objectives

- To extract cellulose from waste paper
- To prepare silica nanoparticles in the form of silica sol
- To synthesize and characterize cellulose-silica nanocomposites from both purified cellulose fibers and cellulose nanoparticles derived from waste paper
2.0 LITERATURE REVIEW

2.1 Cellulose

Cellulose is a highly unbranched polymer of β-1,4-linked D-glucose (refer to Figure 1) extensively found in plant cell wall alongside hemicellulose and lignin. The percentage content varies according to the species, surrounding environment, and maturity (Kong, 2011). Each chain is connected through strong intra- and intermolecular hydrogen bonds, giving a highly crystalline structure.

![Molecular structure of cellulose](Figure 1: Molecular structure of cellulose (Ying, 2008, p. 6)

The broad network of hydrogen bonds and partial crystal structure, however limit the solubility of cellulose in water or organic solvents (Cai & Zhang, 2005). Known suitable solvent systems have to be prepared ahead are such as that of N-methyl morpholine N-oxide (NMMO) (Fink, Weigel, Purz, & Ganster, 2001), lithium chloride/1,3-dimethyl-2-imidazolidinone (LiCl/DMI) (Takaragi, Minoda, Miyamoto, Liu, & Zhang, 1999), and phosphoric acid (Northolt et al., 2001). The solubility would largely rely on the breaking of inter- and intra-molecular hydrogen bonds. Another solvent that can be used and which will be used in this study is the NaOH/urea aqueous solution. It can dissolve cellulose without heating.
(Cai and Zhang, 2005), and is economically and environmentally friendly (Qi, Chang, & Zhang, 2009).

2.2 Type of Cellulosic Materials

Cellulosic materials have gained attention and been developed extensively over the past decade for their environmentally friendly property. Agricultural residues and wastepaper have been efficiently used to bring about composites made of cellulose and organic or inorganic particles. These composites are synthesized with either reinforced or synergic desired properties.

Roger (2008) utilized cellulose from coconut husk of species *Cocos nucifera* and banana peels. Coconut husk is reported to contain 90% cellulose and lignin, and is suitable for ion exchange purposes (Yun, 2004). Banana peels has the highest cellulose content among fruits, with antifungal and antibiotic properties in the peels and pulp (Roger, 2008).


Paper consists of 90-99% cellulose with adjacent hydrogen bonds connecting each fiber (Kong, 2011). Cotton linter is the remaining fiber following cotton ginning, and is a side product of oil mill production (Kong, 2011). Cotton wood has about 40-55% cellulose (Mohd Yusof, 2008). Other examples of plants include banana trunk (Meor Mohd Lani, 2012), corn cob (Samsudin, 2009), rice straws (Shafie, 2012), native tapioca and corn starches (Wong, 2004),
sugar cane bagasse (Ahmad Yarani, 2009), wood, and crop waste (Hubbe, Rojas, Lucia, & Sain, 2008).

Bacterial cellulose such as those from the genera *Acetobacter, Agobacterium, Alcaligenes, Pseudomonas, Rhizobium,* or *Sarcina* (El-Saied, Basta, & Gobran, 2004) does not require chemical pretreatments as they do not contain lignin and hemicellulose (Barud et al., 2008). Czaja, Romanovicz, and Malcolm Brown (2004) reported potential application of bacterial cellulose in medicine for burns. It can also be used to obtain cellulose whiskers, besides wheat straw and tunicin (Mohd Yusof, 2008).

### 2.3 Cellulose Pretreatment

Pretreatment is done to extract cellulose from lignocellulosic compounds. An ideal pretreatment is one that breaks lignin, hemicelluloses and cellulose structure (Brodeur et al., 2011). However, each pretreatment has its own shortcomings in removing lignin and attaining pure cellulose. As different pretreatments can give different results, some researchers combine two or more methods.

#### 2.3.1 Mechanical pretreatment

Milling is one of the most common mechanical pretreatment. This method is used when requiring smaller particle size to increase surface area or lowering the crystallinity of cellulose (Kumar, Barrett, Delwiche, & Stroeve, 2009). It is relatively expensive, similar to grinding.

#### 2.3.2 Chemical pretreatment

The most common chemicals used in alkaline pretreatments are sodium, potassium, calcium, and ammonium hydroxide. They function to break and reduce the bonds strongly held in lignin.
Sodium and calcium hydroxide need not require extreme conditions to increase the solubility of lignin. Ammonia, on the other hand, demands higher temperature but is relatively lower than other pretreatment methods (Mosier et al., 2005). The reaction time, however is longer. Cellulose swelling is a side effect, but it helps in removing inks on printed paper (Bajpai, 2013) and solubilizes pectin and hemicellulose as the swollen fibers have larger surface area and more susceptible to chemical treatments (Sun & Cheng, 2002).

Acid hydrolysis is one of the techniques that is frequently used, with sulfuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), phosphoric acid (H$_3$PO$_4$) and nitric acid (HNO$_3$) as examples. Acids in dilute concentration are enough to separate and recover hemicellulose (Kumar et al., 2009). Nevertheless, they are toxic, corrosive and hazardous, requiring precautions that are costly. Acids are more effective in lignin removal than alkaline treatments but prolonged treatment will degrade and decrease cellulose yield (Brodeur et al., 2011). Combining with alkaline pretreatment, which is able to break down lignin, it serves as an alternative in obtaining pure cellulose (Brodeur et al., 2011). Thorough washing will be needed after pretreatment to neutralize the cellulose.

Organosolv consists of one or more organic solvents with water. Examples include ethanol, methanol, acetone, ethylene glycol and tetrahydrofurfuryl alcohol (Kumar et al., 2009). Acids can be added as catalysts to break lignin and hemicellulose (Sun & Cheng, 2002). There have been numerous researches reporting the use of acetic acid pulping that successfully degrade wood and other cellulose derivatives (Ahmad Yarani, 2009). To reduce the expense and possible pollution, the solvent needs to be separated and recovered after treatment (Harmsen, Huijgen, Bermúdez López, & Bakker, 2010).
Oxidative delignification uses an oxidising agent such as hydrogen peroxide, ozone, oxygen or air in the presence of enzyme peroxidase. This technology can also remove some hemicellulose (Harmsen et al., 2010). Hydrogen peroxide gives the highest yield whereas ozonolysis does not affect hemicellulose and cellulose. Adding water to oxygen or air, wet oxidation at extreme conditions can successfully disrupt the rigidity of hemicellulose and lignin (Panagiotou & Olsson, 2007). A study conducted by Kumar et al. (2009) showed that the combination of wet oxidation and alkaline pretreatment on wheat straw gave 85% yield. The combination produces a bleaching effect as well (Menezes & Choudhari, 2011).

2.3.3 Biological pretreatment

As it does not involve extreme conditions and expensive equipments, the use of naturally occurring decomposition process is used by some researches as well. Microorganisms excrete enzymes peroxidase and laccase to break down lignocellulosic materials (Lee et al., 2007). Biological treatment was used alongside with organosolv by Itoh, Wada, Honda, Kuwahara, and Watanabe (2003). The process consumed only water, ethanol, fungi and 15% less electrical energy. The time taken, however, is extremely slow.

2.4 Cellulose Dissolution

2.4.1. Viscose method

This method was first discovered by Charles Frederick Cross, Edward John Bevan, and Clayton Beadle in 1894 to produce artificial silk (Bunsell, 2011). It is made of carbon disulfide, CS₂ in alkaline conditions. Adding cellulose will give a highly viscous xanthate solution. The first step is soaking cellulosic materials in alkaline solution to convert native cellulose to alkali-cellulose.
Cell−OH + NaOH $\rightarrow$ Cell−O$^-$ Na$^+$ + H$_2$O

Cellulose chains become swollen from the alkaline treatment for easy degradation of high degree of polymerization (Moulijin, Daamen, O’Connor, & Meij, 2011) to achieve desired viscosity of viscose solution. The next step is xanthation by adding CS$_2$.

$$\text{Cell}−\text{O}^−\text{Na}^+ + \text{CS}_2 \rightarrow \text{Cell}−\text{O}−\text{C}−\text{S}−\text{Na}^+$$

The cellulose xanthate is then dissolved in dilute alkaline solution by breaking intra- and intermolecular hydrogen bonds of cellulose chains (Moulijin et al., 2011).

$$\text{S}$$

$$\text{Cell}−\text{O}−\text{C} + \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Cell}−\text{O}−\text{C}−\text{OH} + \text{H}_2\text{O}$$

$$\text{S}−\text{Na}^+$$

The advantage of this solvent is the ability to dissolve cellulose in the presence of lignin (Ying, 2008). However, the reagents used (CS$_2$) and produced (hydrogen sulfide, H$_2$S) creates environmental pollution (Ingildeev, Effenberger, Bredereck, & Hermanutz, 2013).

2.4.2 Cuprammonium process

In 1937, Schweizer successfully dissolved cellulose materials such as cotton and hemp in a mixture of copper hydroxide and ammonium hydroxide solution (Zhang, 2014). The dissolution process occurs by complexation between cuprammonium, Cu(NH$_3$)$_4^{2+}$ ions and the hydroxyl groups of cellulose (Zhang, 2014). Although higher degree of polymerization
cellulose can be used for this system compared to viscose process, the environmental problems of by-product copper sulfate lead to reduced favorability by manufacturers (Kotek, 2007).

2.4.3. N-methylmorpholine-N-oxide (NMMO)

Also known as the Lyocell solvent (Brodeur et al., 2011), it was considered as one of the best system in dissolving and producing high concentration of cellulose. Current findings that still went with NMMO to regenerate cellulose are those by Shanshan, Jianqing, and Zhengwei (2012), and Dogan and Hilmioglu (2009). The results showed that there were reduction in the crystallinity and crystal size, but the thermal stability, mechanical and barrier properties of the regenerated cellulose improved. Dogan and Hilmioglu’s study included the use of microwave heating. It did not show any effect on both degrees of polymerization and crystallinity, proving it as a more efficient way to dissolve cellulose. Calvin (2001) traced the use of a derivative of the solvent, cyclic mono-NMMO in reinforcing paper back to 1969. The solvent is synthesized by adding n-propyl gallate to NMMO. It has been acknowledged that the method chosen is green, nontoxic and recyclable (Gao, Shen, & Lu, 2011). However, the production of NMMO is not favorable as it is cost-consuming, unstable, and difficult to recover (Zhu et al., 2006).

2.4.4 N, N-dimethylacetamide (DMAc)/ Lithium chloride (LiCl)

This solvent system was first discovered by McCorrnick and is favored when involving homogenous modification and analytical works (Olsson & Wesman, 2013). To synthesize, DMAc is refluxed with nitrogen in air before cooling and adding LiCl. As a nondegradable solvent, its function stretches to those of high molecular weight polymers with minimum alteration. The system demands a cellulose and solvent water-free maintenance to prevent alterations from water impurities (Potthast et al., 2002). The solute will then be better able to
bond with other molecules. This is time-consuming and cellulose interaction is limited in this solvent system.

### 2.4.5 Aqueous solution

Egal (2006) discovered that the addition of urea in NaOH has begun in the late 90s using cellulose with high degree of polymerization. Zhang, Li, Yu, and Hsieh (2010) reported an alternative for urea: thiourea. Even though NMMO/H₂O solvent gives the highest efficiency in dissolving cellulose, NaOH/urea and NaOH/thiourea are able to function without high temperatures (Zhang et al., 2010). Qi et al. (2009) conducted a study on the varying temperatures in cellulose dissolution, showing an increase in solubility of cellulose when the temperature decreased. The solvent gave a maximum dissolution at −12.6°C, despite the longer time needed. The low temperature prevents degradation of cellulose and evaporation of the chemicals used, thus regarding them as a green solvent (Lue, Zhang, & Ruan, 2007). The elasticity and mechanical properties of the cellulose were maintained as before (Ruan, Zhang, Zhou, Jin, & Chen, 2004). Liu and Zhang (2009) found that the combination of urea and thiourea in an alkaline solution will increase cellulose dissolution process. Overall, it is a cheap, simple, and green solvent. The limitation in industrial application is one of the drawbacks (Zhang, Ruan, & Gao, 2002).

### 2.4.6 Ionic liquids

Ionic liquid is made of salts of very low vapor pressure, low toxicity, low viscosity and high stability (Brodeur et al., 2011). It has garnered attention due to its role as a solvent for different types of biomass. The vast possibilities of anion-cation pairs with desired properties give ionic liquid a versatility applicable in different fields. The most frequent cations used are