A high strength green nanocomposites based on wood veneer nanocrystalline cellulose and epoxy resin polymer

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Abstract. This study was conducted to utilize natural thin wood veneers, nanocrystalline cellulose (NCC) and epoxy resin to produce new bionanocomposites. The thin wood veneers were used as the basic structure element in the nanocomposites. The NCC was obtained from the chemically hydrolyzed sawdust with diameter of ~10-20 nm. In this study, NCC was mixed with 3-glycidyloxypropyltrimethoxysilane (GPS) before being dispersed homogeneously into the epoxy resin and thin veneer. The GPS which act as the coupling agent enhanced the interfacial adhesion between NCC and epoxy resin polymer. The Fourier Transform Infrared Spectroscopy (FTIR) results showed that NCC was successfully treated with GPS. The finding showed that the optimum value of GPS solution required to functionalize NCC was 0.5 wt/wt %. The results on tensile strength tests on the green nanocomposites also showed that the strength improved upon the incorporation of treated NCC into epoxy resin and thin veneer. By incorporating treated NCC (0.1%) into the thin wood veneer/epoxy resin polymer based nanocomposites, the maximum increment value of tensile strength was found to have a 23% improvement compared to the control sample without NCC. The enhancement in the strength properties was expected as NCC possessed high surface-to-volume and aspect ratio characteristics. Through this study new high strength green nanocomposites have been successfully developed.

1. Introduction

Nanotechnology offers potential opportunities for development of advanced wood- or lignocellulosic-based biocomposites. It is an alternative tool to manipulate and control processes and materials at nanoscale level. The technology is currently leading to new analytical technologies that provide a fundamental understanding of material behaviour at the nanoscale. It includes the incorporation of nanomaterials into biocomposites to achieve enhanced performance of the final products. It also leads to modifications of the wood and lignocellulosic raw material surfaces at the nanoscale. By exploiting these potential opportunities to identify, control, optimize material and process factors in real-time, products can be engineered to have highly specified performance characteristics with economic advantages. Nanocrystalline cellulose (NCC) is cellulose in crystalline form, which is extracted from biomass and processed into several forms such as solid flake, liquid and gel. The lateral dimension of nanocrystals is in the order of 10-100 nm and the length can be in the micrometer scale, both parameters depending on the preparation method [1]. Unlike other nanomaterials, NCC manufacturing is already a sustainable and viable bulk process. NCC can be generated in a vast amount each day, producing other

viable by products such as glucose (for alternative fuel) and gypsum (for buildings) and their mechanical performance compares well with other materials [2-3]. Several main properties such as high strength, electro-magnetic response and a large surface area provide a basis for the manufacture of new and advanced materials using nanotechnology.

Over the last few years, there has been a great deal of interest in research and development works on nanocomposites in Malaysia. NCC is considered as one of the ideal nano-reinforcements for matrices (including water-soluble and water-insoluble polymer systems) and has already been incorporated into many polymer matrices to produce highly reinforced composites [4-5]. Epoxy resins denote to a class of polymeric materials whose applications are extensive and range from coatings, to adhesives to composite materials for electronics, sporting goods and others [6]. The inclusion of nanofillers into epoxy resins can lead to a combination of high stiffness and strength, and good fatigue resistance [7]. The use of NCC as reinforcing fillers in epoxy resins have been reported from previous studies. Rusli and Eichhorn (2008) investigated the stiffness of cellulose whisker/epoxy system using Raman spectroscopy and highlighted the importance of the interface between matrix and nanofiller [8]. Lu et al. (2008) recently reported that the modulus increased approximately 6 fold upon incorporation of 5% w/w microfibrillated cellulose into an epoxy matrix [9].

As worldwide demand for timber and lignocellulosic resources grows in order to compete with the needs of rapidly increasing populations, the management of this sustainable resource becomes a critical issue. There is a need to fully utilize the natural wood efficiently. Wood veneer refers to thin slices of wood, usually thinner than 3 mm and typically obtained by shaving, peeling or slicing thin layers of wood off a suitable log. These wood veneer products are commonly used as decorative surfacing for furniture, interior and exterior components of automobiles. Typically, fused decorative products for furniture and automotive applications are made by bonding thin sheets of high-quality wood to a core material such as plywood, metal or particleboard. The thin veneer (with average thickness – 0.3 mm) by its own, exhibits relatively poor strength. Hence, this study attempted to utilize natural wood veneer as a basic structure element in producing a new type of green nanocomposite. The aim of this study was to investigate the contribution of the NCC reinforced epoxy polymer properties and its bonding/network structure to the overall properties of the produced nanocomposites. By incorporating NCC, enhancement in strength property is expected as NCC possesses high surface-to-volume and aspect ratio characteristics to ensure effective incorporation with the veneer matrix. Silane was used as the coupling agent to promote interfacial adhesion via chemical bonding which is stronger compared to the possibly occurring hydrogen bonding between the hydrophilic functional groups, leading to the improvement of the composite properties.

2.   Materials and Methods

2.1   Materials and chemicals
Sawdust was used as the raw material in producing NCC. Glycidyloxypropyltrimethoxysilane ≥98 % (GPS) and epoxy resin were produced by Sigma-Aldrich. Ultrathin wood veneers utilized in this study were supplied by a nearby supplier. All other chemicals used were purchased from Merck (M) Sdn. Bhd. The chemical structures of GPS ($C_9H_{20}O_5Si$) and epoxy resin are illustrated in Fig.1.
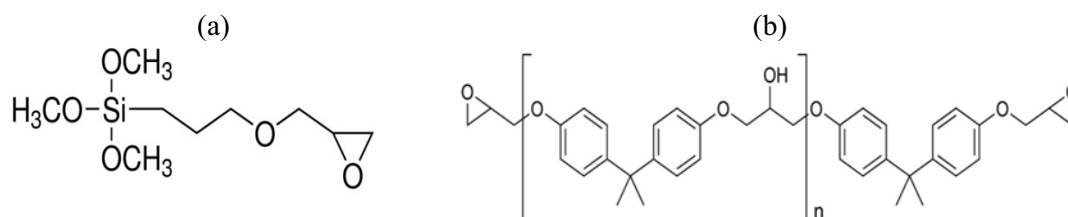
Figure 1. Chemical structures of (a) GPS and (b) epoxy resin.

2.2   Surface treatment of NCC

Nanocellulose was produced from sawdust using acid hydrolysis method reported elsewhere [10]. The solution was prepared by addition of 5 wt. % GPS, drop by drop to water- ethanol (80/20) (v/v %) under stirring. The pH of the solution was adjusted to 3~4.5 with diluted acetic acid to catalyze the hydrolysis process. Silane solution was stirred for 15 min and left for 1 hour to allow complete hydrolysis of the silane. After complete hydrolysis and silanol formation, NCC was dipped in solution and sonicated for 10 minutes to prevent the aggregation of NCC and to produce homogenous suspension. The suspension retained for two hours at room temperature. The suspension was then washed with distilled water using centrifuge to remove any excess silane from the NCC before lyophilization.

2.3   Production of NCC reinforced epoxy resin polymer and thin veneer
Treated NCC was dispersed in the curing agent of epoxy resin system (hardener). The mixture was sonicated to produce homogenously suspension. The admixture was then added into epoxy resin and stirred uniformly.

The treated NCC-epoxy polymer admixture was integrated into the thin veneer. The thin veneer was oven dried at 60°C. The treated NCC-epoxy admixture was cast on the veneer and distributed uniformly by hand roller. The treated veneer was pressed using cold press for 24 hours at 200 psi. Then, the veneer laid at ambient room temperature for curing process. A similar technique was used for the untreated NCC reinforced epoxy resin polymer/thin veneer composites. Nanocomposites with different untreated and treated NCC contents were prepared.

For comparison, the nanocomposite samples without the thin wood veneer were also prepared. The NCC-epoxy admixture was poured into a mold with dimensions of 170 mm x 170 mm x 3 mm and left cured at room temperature. These nanocomposites were produced using treated and untreated NCC, respectively.

2.4   Characterization

2.4.1   Fourier transforms infrared spectroscopy (FTIR). Each sample was mixed homogeneously with potassium bromide (KBr) and ground into powder using a mortar and a pestle. The mixture was transferred into a mold and was hydraulic pressed to form a 13 mm diameter KBr disc. The FTIR spectra were recorded in the range of 4000 to 450 cm^{-1} with a total accumulation of 16 scans employing a Perkin Elmer Spectrum 100 Series. All samples were analyzed in triplicate.

2.4.2   Tensile test. Tensile testing was carried out using Instron Universal Testing Machine according to ASTM D 638-91 with a cross head speed of 5 mm/min. The specimens were cut to dimensions of 160 mm x 13 mm. The tensile values were taken from an average of 10 specimens.

3.   Results and Discussion
The nanocomposites investigated in this study were based on an epoxy resin formed by the reaction of an oligomeric difunctional diglycidyl ether of bisphenol A with an epoxide equivalent weight of 185-192 and a diethyl toluene diamine-based curing agent in the presence of wood veneer and NCC isolated from sawdust.

3.1   Fourier transforms infrared spectroscopy
FTIR analysis in Figure 2 attempted to characterize the spectra for NCC, GPS and treated NCC. The absorbance peaks in the range 3400-3300 cm^{-1} are attributed to the stretching of the OH groups of cellulose. The peaks observed around 2905 - 2899 cm^{-1} corresponds to C-H stretching in the spectra of both NCC and treated NCC [11]. The peaks at 1640–1650 cm^{-1} attribute to C=C stretching. The spectrum for treated NCC show absorbance at 1100–1200 cm^{-1} is Si –O-Si and Si-O-C stretching. GPS shows a strong absorbance at 845-820 cm^{-1} is C-O-C stretching vibration of epoxy ring. The peak at 1083 cm^{-1} is from the Si-O-CH$_3$ strong stretching vibration. The peaks observed around 1275- 1255 cm^{-1} corresponds to C-O-C stretching in the spectra of GPS. The strong absorbance of GPS shown in the treated NCC spectrum clearly indicates that NCC is successfully treated with GPS.
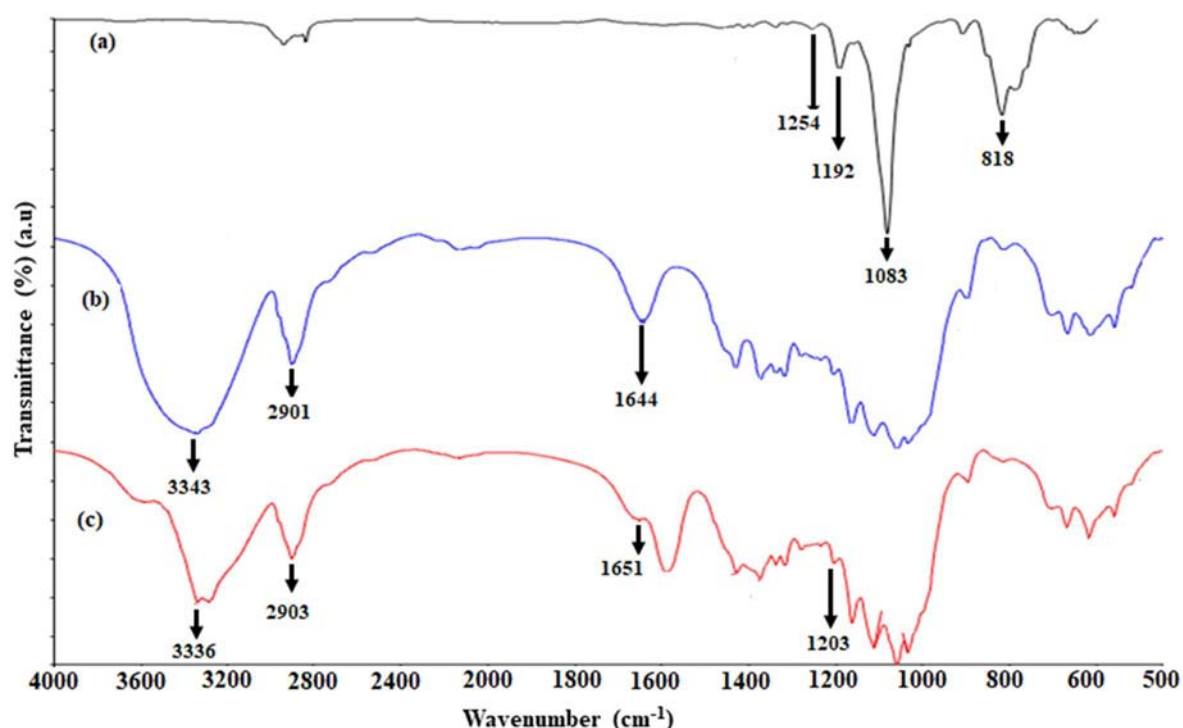
Figure 2. FTIR spectra of (a) GPS, (b) NCC and (c) treated NCC (NCC-GPS).
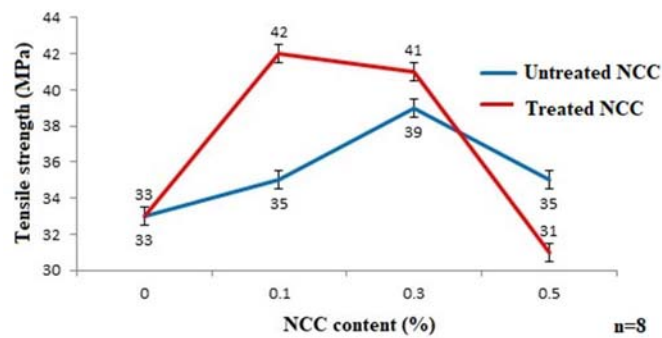
3.2   Tensile properties

The addition of GPS was to improve the compatibility and dispersion of nanocellulose into the polymer matrix. The tensile properties of the epoxy resin reinforced with GPS treated NCC composites are shown in Figure 3a. The finding shows that the tensile strength of the nanocomposites improved after modification with silane. The highest value is about 42 MPa at 0.5 wt/wt % of GPS solution utilized to treat NCC. The change in tensile strength is not significant for the nanocomposites with 1 wt/wt % of GPS solution compared to 2% wt/wt % of GPS solution after which it decreased. The advantages of silane coupling agents are: (i) they are commercially available in a large scale; (ii) they have alkoxysilane groups capable of reacting with OH-rich surface at one end, and (iii) at the second end, they comprise a large number of functional groups which can be tailored as a function of the polymer to be used. This is to ensure a good compatibility between the reinforcing element and the polymer or even develop covalent bonding between them [12].
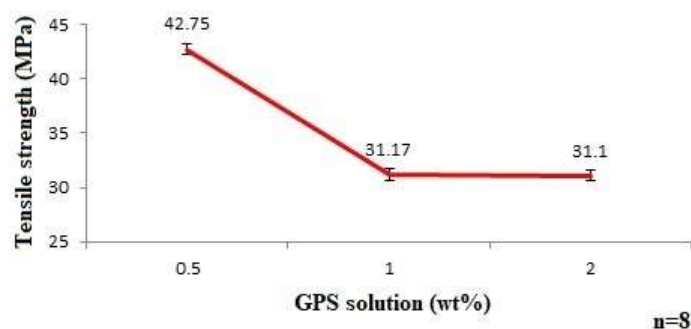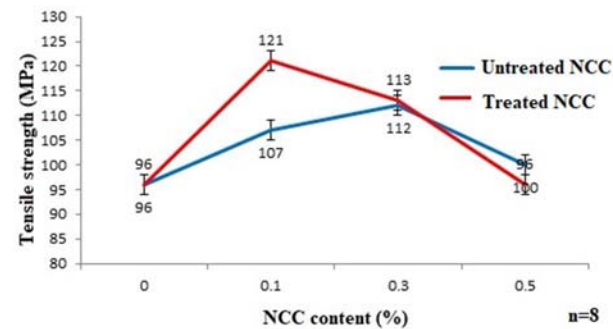

3(a)
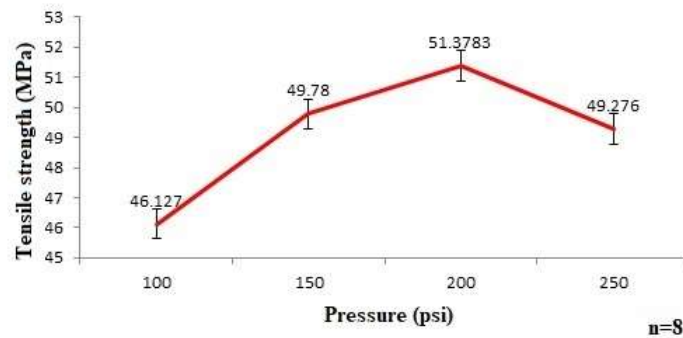
3(b)

3(c)

3(d)

Figure 3. (a): Tensile properties of nanocomposites at different percentage of GPS utilization. 3(b): Tensile properties of nanocomposites at different pressing pressure. 3(c): Tensile properties of untreated and treated NCC reinforced nanocomposites. 3(d): Tensile properties of untreated and treated NCC-epoxy resin polymer reinforced ultrathin wood veneer nanocomposites.

The effect of pressing pressure on tensile properties of nanocomposites produced is indicated in Figure 3b. The finding shows that the range between 150 to 250 psi is the ideal pressure range to develop the harmonized cured NCC reinforced epoxy resin polymer/thin veneer composites. The rigidity of this harmonized nanocomposite helped in distributing uniformly the force applied onto the nanocomposites. The result shows the optimum value of tensile strength is at 200 psi, with an 11.3 % improvement.

The finding in Figure 3c shows the comparison results between untreated NCC-epoxy resin composites and treated NCC reinforced epoxy resin composites. The tensile strength of neat epoxy resin was found to be 33.7 MPa and the reinforced composites with addition of 0.1 (w/w) treated NCC enhanced the tensile strength values up to 42.4 MPa before started to decrease to 41.2 and 30.9 MPa as the loading value increased, 0.3 and 0.5% respectively. The maximum increment value of tensile strength was found at 0.1 wt. % filler loading with a 26% improvement. On the other hand, the addition of untreated NCC into epoxy resin polymer has improved the tensile strength by a factor of 17% at 0.3

wt.% filler loading, Hence, the result reveals that the treatment of NCC using silane contributed to the improvement in interfacial bonding between the NCC and epoxy resin polymer [13-14]. This is due to the optimum reinforcing effect for the treated NCC in the nanocomposites was distinctly developed using lower amount of NCC content (0.1 wt.%) as compared to the untreated NCC content (0.3 wt.%) in the nanocomposites.

The effect on the tensile strength of untreated and treated NCC incorporated in ultrathin wood veneer-epoxy resin based composites was observed as a function of the NCC loading ranging between 0.1 and 0.5% (w/w) (Figure 3d). The thin wood veneer was used as the basic structure element in the nanocomposites. Similar finding was found for the optimum reinforcing effect for the untreated and treated NCC incorporated into thin wood veneer-epoxy resin based composites. The tensile properties of treated NCC incorporated into thin wood veneer-epoxy resin based composites increased by 23% at the optimum NCC loading of 0.1 wt. %. Whereas the addition of untreated NCC untreated into ultrathin wood veneer-epoxy resin based composites shows the increment of 22% of tensile strength at 0.3 wt.% NCC content. Beyond the optimum NCC loading, the tensile strength values plateau suggesting that the addition of more NCC above this threshold concentration does not help to improve the tensile properties. The reason for the value to plateau may be due to the potential aggregation of NCC particles after a certain concentration is reached, which results in no further improvement of mechanical properties.

4.   Conclusion

Nanocrystalline cellulose (NCC) has a high aspect ratio characteristic that will improve the mechanical property of polymers. However, because of the hydrophilicity of NCC, it has to be modified chemically or physically to achieve the desired interfacial adhesion between the filler and the hydrophobic matrix. In this study NCC has been treated by 3- glycidoxylpropyltrimethoxysilane (GPS). The additions of treated and untreated NCC into epoxy resin based composites with and without thin wood veneer have improved the strength properties of the nanocomposites compared to the neat epoxy resin system. However, the addition of treated NCC rather than untreated NCC resulted in higher tensile. At low amount of NCC content (0.1%), the maximum increment values of tensile strength of thin wood veneer/epoxy resin polymer based nanocomposites was found to have a 23% improvement compared to the control sample without NCC. These green nanocomposites have the potential to be utilized to produce high strength laminated composite engineered products.

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