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PREPARATION AND CHARACTERIZATION OF WOOD/CERAMIC NANOCOMPOSITES AND THEIR POTENTIAL WOOD PROTECTION APPLICATIONS.

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DECLARATION

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

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Preparation and Characterization of Wood/ceramic Nanocomposites and Their Potential Wood Protection Applications.

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ABSTRACT

This research focused on the preparation and characterization of wood/ceramic nanocomposites using metal oxide sols and selected wood samples. The metal oxide sols were prepared by the sol-gel technique. Wood/ceramic nanocomposites were prepared by submerging wood samples into the metal oxide sols under controlled conditions. Besides, the effectiveness of metal oxide nanoparticles for wood preservation was also being studied. Established characterization techniques using instruments such as Fourier Transformed Infrared Spectrometer (FTIR), Scanning Electron Microscopy (SEM), Optical Microscope and CHN Analyzer were used to characterize the wood/ceramic nanocomposites prepared under various conditions. Visual rating scale for decay and termites' attacks were used to evaluate the effectiveness of selected metal oxides nanoparticles for wood preservation study.

Key words: Wood/ceramic nanocomposites, wood preservation, metal oxide sols, sol-gel technique.

ABSTRAK

Fokus bagi kajian ini melibatkan penyediaan dan pencirian nanokomposit kayu/seramik menggunakan sol logam oksida dan sampel kayu yang terpilih. Sol logam oksida disediakan menggunakan teknik sol-gel. Nanokomposit kayu/seramik disediakan dengan cara merendamkan sampel kayu di dalam sol logam oksida di dalam keadaan terkawal. Di samping itu, keberkesanan nanopartikel logam oksida untuk pengawetan kayu juga dikaji. Pencirian mapan, teknik menggunakan Spektrometer FTIR, Mikroskop Imbasan Elektron (SEM), Mikroskop Optikal dan Penganalisis CHN digunakan untuk mencirikan nanokomposit kayu/seramik yang disediakan di dalam keadaan terkawal. Skala kadar visual digunakan untuk menilai keberkesanan nanopartikel logam oksida terpilih terhadap serangan pereput dan anai-anai untuk kajian pengawetan kayu.

Kata kunci: Nanokomposit kayu/seramik, pengawetan kayu, sol logam oksida, teknik sol-gel.

1. Introduction

Nanoparticles have become a very exciting field of research since 1980s. Scientists are interested to synthesize and develop of new materials with nanoscales particles sizes from 1 to 100 nm and investigate their potential applications due to their smaller size (Diwan and Bharadwaj, 2006). Studies have shown that the properties of the materials on the nanoscales are different from those on the bulk scale, so nanoparticles can be used to improve and produce much better products (Ke and Stroeve, 2005).

Sarawak has a very large area of about 12.3 million hectares and about 85% of this area is covered by natural forest. The forest contains a variety of timber species such as Kempas (*Koompassia malaccensis*), Tualang (*K.* e*xcelsa*), Keruing (*Dipterocarpus spp.*) and so on. The unique characteristics and versatility of wood derived from these timber species provides extensive uses of wood and wood products (Wong *et al*., 1997). However, the products of wood must be protected from being attacked from the biodegradation organisms like sapstain, decay fungi, harmful insects or termites. There were conventional heavy metals has been used nowadays as wood preservatives such as copper-chrome-arsenic (CCA), copper-chrome-boron (CCB) and tin (Sn) (Wong and Choon, 2007; Wong and Pearce, 1997). This study is carried out to produce metal oxides nanoparticles that can be more effective wood preservatives and safer towards human health.

Nanocomposites are one of the nanomaterials that can be derived from nanoparticles. The research of nanocomposites has become more significant to industrial nowadays. Their unique properties such as resistance to heat and radiation aging, posses the characteristics of smooth surfaces and able to kill bacteria has contributed to the development industry of producing nanocomposites coatings (Ke and Stroeve, 2005).

In this research, wood/ceramic nanocomposites will be prepared under controlled conditions. Some of the characteristics and cellular structure of the wood such as the porosity and the absorptivity of wood will be studied. The wood/ceramic nanocomposites formed will be characterized by using Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscopy (SEM), Transmission electron Microscopy (TEM) and CHN analyzer. The characterizations of the nanocomposite include their size and shape of particles, surface morphology and crystal structures. Besides, the wood/ceramic nanocomposites will be investigated on their potential applications as wood preservatives. All the methods will be discussed further in the methodology.

Among research objectives of this study includes:

1. To prepare wood/ceramic nanocomposites using selected metal oxides nanoparticles and wood samples.
2. To characterize wood/ceramic nanocomposites prepared under controlled conditions.
3. To evaluate the effectiveness of selected metal oxides nanoparticles for wood preservation.

2. Literature Review

2.1 Nanoparticles and Nanocomposites

2.1.1 Nanoparticles

Nanoparticle is a particle with nanoscales within nanometers that is less than 100 nm (Ke and Stroeve, 2005). Polarz *et al.* (2002) stated that, the advanced technologies of nanoparticles molecules separation and catalytic conversion for the materials have become increasingly significant nowadays. The studies deal with the synthesis, characterization, exploration and exploitation of nanostructured materials (Rao *et al.*, 2004; Rao and Cheetham, 2001).

There are many techniques have been used to characterize the nanoparticles of materials in the previous research. The techniques used are included Auger Electron Spectroscopy (AES), Low Energy Ion Scattering (LEIS), Secondary Ion Mass Spectroscopy (SIMS), X-Ray Photoelectron Spectroscopy (XPs), electron microscopy of different types, thermal and desorption spectroscopy (Otterstedt and Brandreth, 1998).

2.1.2 Nanocomposites

Nanocomposites are materials that are produced by introducing the nanoparticles into a macroscopic sample material that may results in the properties improvement like electrical and thermal conductivity, optical properties, dielectric properties or mechanical properties such as strength and stiffness. The properties of nanocomposites materials and the corresponding microcomposites are significantly different that are the stiffness and strength of nanocomposites is highest (Ng *et al*., 2001; Yano *et al*., 1993). Lee *et al*., (1999) stated that, ceramic nanocomposites exhibit the increase of the fracture toughness. Composite is a combination of two or more materials with multiple phases and different chemical and physical properties formed by filling, blending, compounding, mixing, melting and assembling (Ke and Stroeve, 2005; Zhang and Mo, 1994). A nanocomposite in organic-inorganic composites refers to composites in the inorganic phase which has nanoscale morphology such as fibers, particles and tubes (Ke, 2003; Zhang and Mo, 1994).

New applications of nanocomposites coatings such as shape shielding coatings, printing of integrated circuits, barrier coatings, wave-absorbing coatings and sonic-insulating coatings has been applied in industrial. The unique properties such as resistance to heat aging and radiation aging, posses the characteristics of smooth surfaces and able to kill bacteria make them became more important to industrial (Ke and Stroeve, 2005).

2.2 Metal Oxide Sols

The selected metal oxides nanoparticles in the preparation of sols in this study are silicon dioxide (SiO_2) and titanium dioxide (TiO_2). Sol means the homogeneous suspending solution containing nanoparticles. Sol gel technique is the efficient process for producing metal oxide nanoparticles with thin, transparent, multi-component oxide layers of many compositions on a variety of substrates (Brinker and Scherer, 1990; Interrante and Hampden-Smith, 1998; Hamid and Rahman, 2003). According to Ke and Stroeve (2005), the properties of nanometer additives included low loading amount for polymers, low coefficients of heat resistance and low in specific weight changes are interesting. The molecular level of composites formed between the polymer matrix and nanoparticles resulted to the super transparency obtained from nanoparticles.

2.2.1 Silicon Dioxide (SiO_2) sol

Silicon dioxide is also known as silica. It is the oxide of silicon and is a main element of most types of glass and substances like concrete. According to Ke and Stroeve (2005), by using a number of techniques, nanoparticles of prepared layered silicate and silica can be modified to form intermediate materials. The formations of intermediates are important to make sure that they are being endowed with good dispersion behavior and desirable functional properties such as catalytic, radiation shielding, optical and barrier properties. There are several aspects involved in the modification of particles such as preparation, synthesis and mechanical blending.

Tetraethylorthosilicate (TEOS) acts as an intermediate reagent or precursor in the preparation of silica particles through sol gel process. Silica became more important to industrial and has been applied to produce composites with rubber, resins, nanocomposites and fibers. Nowadays, silica is used in fields such as electronic components, coatings, engineering plastics and automobile tires.

2.2.2 Titanium Dioxide (TiO_2) Sol

Titanium dioxide (TiO_2) is also known as titania. According to Judin (1993), titanium dioxide (TiO_2) with a particle size below 100 nm that is also called as 'ultrafine' titanium dioxide (TiO_2) has a wide spread applications in elevated efficacy sun creams as an inorganic sun block. Chrysicopoulou *et al.*, (1998) stated that, titanium dioxide (TiO_2) sol have received much attention research as their chemical stability, high refractive index and high dielectric constant that allowed their uses as a components in optoelectronic devices, photocatalysis and sensors.

Granqvist (1995) said that, the titanium dioxide (TiO_2) sols have the ability to change their optical properties in a reversible and consistent way under the influence of an external applied potential. By comparing the different methods for the preparation of thin titanium dioxide (TiO_2) electrochromic layer like e-beam evaporation, magnetron sputtering technique, anodization, chemical vapour deposition (CVD) and sol gel technique, it shows that sol gel method has many advantages as it has the possibility of producing large surfaces (Brinker and Scherrer, 1990; Harizanov and Harizanova, 2000; Bell *et al.*, 1994; Granqvist, 1995).

2.3 Samples of Interest

2.3.1 Wood

Wood had been template in order to mimic their specific structures in this research (Shin *et al.*, 2001). The structure of wood tissues is comprised of tracheids (interconnected cells) and lumens (open spaces). The cell walls contain a thin outer layer known as primary wall and thicker inner layer known as secondary wall. Both cells are glued together by the middle lamellae or also known as intercellular layer and they are connected by openings of different shapes and sizes. These openings also called as pits and can be divided into two types of pits; bordered pits and simple pits. Pits act as the communication channels between the cells and contain a pit chamber, a pit aperture and a membrane.

According to Davidson and Freas (1990), tree can be classified into softwood and hardwood. Both softwoods and hardwoods of Malaysian timber have rays and longitudinal parenchyma but the different between them are softwood structures contain tracheids and resin canal while hardwoods contains vessel elements and fibres. However, some softwood is actually harder than some of the hardwoods. The earlywood in the hardwood has a large-diameter vessel early in the season while in the softwood; it has a large and thin-walled tracheid. The hardwood of the latewood has a small-diameter and more compact vessel and thick-walled fibres while softwood has small and thick-walled tracheid. The physical properties of earlywood in most softwoods and ring-porous hardwoods are markedly different from latewood. It is because earlywood is lighter in weight, weaker and softer than latewood. Since latewood has greater density, so it proportion is sometimes used to judge the strength of wood. Organic constituents of wood are cellulose, hemicellulose and lignin. Cellulose is the most important component of wood that constitutes slightly less than one-half of the weight of both hardwoods and softwoods. The proportions of lignin and hemicellulose are varies widely among the species and between the groups of hardwood and softwood.

Wong (1979) said that, since hardwoods are the majority of the timbers available in Malaysia, so the timber trade has been built up are upon these timbers. The Forest Department has introduced a new form of classification that divides the hardwoods into three classes by referring on the density and natural durability of the timbers. The three classes are Heavy Hardwoods (HHW), Medium Hardwoods (MHW) and Light Hardwoods (LHW) and all this classification is now widely used in the country. Wood durability for Heavy Hardwoods (HHW) is greater than 880 kg/m^3 which are categorized as durable wood, about 720-880 kg/m^3 which is categorized and moderately durable wood and Light Hardwood (LHW) is non-durable softwood with a durability less than 720 kg/m^3. The examples for the Heavy Hardwood (HHW) are Tualang (*K. excelsa*), Keruing (*Dipterocarpus spp.*) and Kempas (*Koompassia malaccensis*) while example for Medium Hardwoods (MHW) is like Teak (*Tectona grandis*). For Light Hardwoods (LHW), the examples for this class are like Kelempayan (*Anthocephalus chinensis*), Rubberwood (*Hevea brasiliensis*) and Jelutong (*Dyera costulata*).

2.3.2 Wood/Ceramic Nanocomposites

Wood/ceramic is refers to a porous carbon material with a pipe-cell-microstructure which is similar to the original wood and can be prepared by burning the wood in inert gas at high temperature (Guanjun *et al.*, 2002). The biomorphic ceramics or composites such as SiC, Al_2O_3, TiC, TiO_2 and Si-Mo-C have been prepared from wood/ceramics by the templating technique in the previous research. In example, the hierarchical porous SiO_2-ceramics and TiO_2-ceramics have been prepared from wood structures after high-temperature treatment in air by a surfactant-templates sol gel process (Shin *et al.*, 2001; Sieber *et al.*, 2002a; Sieber *et al.*, 2002b). In this process, the natural grown structures have been used as bulk templates for the fast high-temperature conversion into technical ceramics and composite materials. A new method for the preparation of SiC ceramics derived from natural woods through the reaction between wood/ceramics and silicon dioxides at high temperature also has been developed (Pavon *et al.*, 2005; Guanjun *et al*., 2002; Cao *et al*., 2004; Hou *et al.*, 2007).

2.3.3 Wood Preservation

Wood preservation is the wood treatment method or process applied to the solid wood or wood composites by using chemicals that can prevent them from being attacked by biodegradation organisms like sapstain, decay fungi, harmful insects or termites. Wood composites can be defined as a mixture or combination of two or more materials together to form something as a product like particle and fibreboards, veneer products, wood and non-wood products. Davidson and Freas (1990) stated that, the degree protection of wood obtained are depends on the type of preservatives used and on the achieving proper penetration and retention of the chemicals. On the other hand, the effectiveness of the preservatives is not only influenced by the protective value of the preservative chemical itself, but also by the method of application and extent of penetration and retention of the preservatives in the treated wood.

A timber or wood preservative should posses all the properties needed to be efficient. The preservatives should be toxic to produce a lethal effect at low concentrations; penetrating the timber to sufficient depth; non-volatile, be chemically stable; non-corrosive on metals; be either liquid or readily soluble in organic solvents or water; be capable of being chemically stable; must not increase the inflammability of timber, must not be deleterious to timber, should not present a major health hazard when in use or when present in the treated product and the most important properties that it must be economic. There are three main types of timber preservatives has been used which are tar oil preservatives, light organic solvent preservatives (LOSP) and water-borne preservatives (Hong, 1994; Hong and Singh, 1985).

Heavy metals like copper-chrome-arsenic (CCA), Tin (Sn) and copper-chrome-boron (CCB) have been used as wood preservative in heavy tropical timber. However, a copper-chrome-arsenic (CCA) preservative is commonly used in the industry of producing wood products. The analysis of copper-chrome-arsenic (CCA) preservative in wood have been done before by using Electron Induced X-ray Emission (EIXE), Proton Induced X-ray Emission (PIXE) (Wong *et al*., 1996) and Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) (Wong *et al*., 1999). This study is suitable in prospect to produce nanoparticles of heavy metals which can be more effective wood preservatives than the conventional heavy metal preservatives such as Copper-Chrome-Arsenic (CCA), Tin (Sn) and Copper-Chrome-Boron (CCB).

3. Materials and Method

3.1 Materials

Wood samples from four wood species of known low natural durability against decay fungi and termites were selected for study. These species were of low to medium wood density. These woods were Terbulan (*Endospermum malaccense*), Kempas (*Koompassia malaccensis*), Kelempayan (*Anthocephalus chinensis*) and Light Red Meranti (*Shorea smithiana*). The average wood density and their preservative treatability are shown in Table 1.

Table 1: The average wood density and preservative treatability of selected wood species.

Wood Species	Average Wood Density (kg/m^3)	Preservative Treatability
Kelempayan	370-465	Good
Terbulan	300-610	Good
Light Red Meranti	385-755	Good
Kempas	770-1120	Good

(A.H.H Wong, Pers. Comm.)

3.2 Preparation of Wood Samples

Wood samples were prepared as shown in Figure 1. For wood/ceramic nanocomposites study, 24 replicates of 1.0 cm cubic of wood samples for each species were used. For wood preservation study, 45 replicates of wood blocks with dimension of 0.5 cm X 3 cm X 10 cm for each species were used. These wood samples were dried in the oven at 103^oC for 48 hours, weighed and recorded.

3.3 Preparation of Metal Oxides Nanoparticles

3.3.1 Preparation of Silicon dioxide (SiO_2) sol

Stable silicon dioxide (SiO_2) sol was prepared based on method shown in Figure 2. About 45 ml of tetraethylorthosilicate (TEOS) was hydrolyzed with a mixture of 10 ml concentrated ammonium hydroxide and 300 ml of Milli-Q water. The two phase system was mixed by stirring or shaking. A stable sol formed when the interface between the two solutions disappears. The silicon dioxide (SiO_2) sol was then being used to treat the wood samples. The sol pH range from 8 to 12 depending on the initial ammonia concentration employed for hydrolysis (S.C. Pang, Pers. Comm.).

3.3.2 Preparation of Titanium dioxide (TiO_2) sols

Procedures for the first preparation method were based on method shown in Figure 3(a). 2 ml of concentrated HNO_3 was added to 277 ml Milli-Q water at room temperature. 23 ml of titanium isopropoxide was added slowly to the acid solution in about 20 minutes. The solution was stirred vigorously and peptized by stirring for 3-4 days. However, this method had failed to prepare stable sol after three preparative trials. No sols which were expected to be transparent, slightly milky and bluish were obtained (S.C. Pang, Pers. Comm.).

The second preparation method was based on method shown in Figure 3(b). 14.9 ml of titanium isopropoxide was added into 180 ml Milli-Q water at room temperature with vigorous stirring. A mixture solution was then added with 1.28 ml of concentrated HNO_3 after the completion of hydrolysis and heated to 108^{o}C. The solution was kept the temperature at 108 ^{o}C for 10 hours to peptize the titanium dioxide (TiO_2) precipitates. The sols form should be transparent which has 100-200 nm aggregates. The sol was then sonicated to reduce the aggregate size of particle to be about 40 nm. However, this method of preparation had also failed to prepare a clear and stable sol as expected (S.C. Pang, Pers. Comm.).

The third preparation method was based on method reported by Hamid *et al*. (2003). Preparation steps involved were shown in Figure 3(c). 1.72 ml of glacial acetic acid was added into 262.22 ml of absolute ethanol. The mixture solution was stirred. After 5 minutes of stirring, 29.92 ml of titanium isopropoxide was then added into the mixture solution and kept stirring vigorously for about 2 hours until transparent sol formed. The pH of titanium dioxide (TiO_2) sol was checked with pH meter to make sure that the sol must be in pH 5. Method 3 was successful in preparing a clear and stable sol which was then used to treat the wood samples in all subsequent studies.

3.3.3 Preparation of Wood/Ceramic Nanocomposites

Wood/ceramic nanocomposites were prepared based on method reported by Shin *et al.* (2007) and as shown in Figure 4. All wood samples were submerged into titanium dioxide (TiO_2) or silicon dioxide (SiO_2) sols which were maintained at 53 ^{o}C for 2 days in an unsealed polypropylene container. The wood samples were then removed from solution and treated similarly in a new solution of titanium dioxide (TiO_2) or/and silicon dioxide (SiO_2) sols for another 2 days at the same temperature. Finally, samples (several pieces of wood on the order of 1.0 cm) were removed from the sol mixture, weighed and dried in the oven at 60 ^{o}C for 3-4 days. The dried treated wood cubes were weighed and then calcined at 550^{o}C for 3 hours in air or/and in nitrogen. The characteristics of wood/ceramic nanocomposites were observed using Scanning Electron Microscopy (SEM), Optical Microscopes, Fourier Transformed Infrared Spectrometer (FTIR) and CHN Analyzer.