

Preparation and Characterizations of Various Clay- and Monomers-Dispersed Wood Nanocomposites

M.R. Rahman and S. Hamdan

Abstract In this chapter, different types of wood polymer nanocomposites (WPNCs) with various clay and monomer were prepared through curing methods, wood-hardening process, and chemical impregnation as well as compression of wood. The samples were ensured to dry at 105 °C up to constant weight before treatment. The dimensions and weights were measured. The samples were undergoing impregnation process in an impregnation vacuum chamber. WPNCs produced were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), compression test, Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM).

Keywords Mechanical properties · Stability · Morphology · Wood polymer nanocomposites

1 Overview

In the past research, many efforts have been applied on the wood reinforcement. Based on the previous literature, it has been clearly showed that the raw wood can be greatly modified and improved its properties through chemical modification. One of the most common and inexpensive techniques developed is in situ polymerization technique on wood polymer nanocomposites (WPNCs). Besides, nanotechnological modification has also been proven to be very effective in improving the various properties of raw wood. From the previous research, there are some research works of polymer/nanoclay system onto wood. Therefore, with the combination of nanotechnological modification and impregnation process, more chemical formulations could be formed and were chosen for this study.

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In this study, there are five types of wood species selected as raw materials as these materials are abundantly available in the local forest in Malaysia. All the selected raw materials are large in quantities but none of them are fully utilized in many applications due to their low qualities in properties. Furthermore, from the literature finding, there was few or no work had been carried out on tropical wood species with various chemicals.

In this study, the experimental work is divided into three sections. The first and second sections included the preparation of wood specimen and the chemical fabrications of wood polymer nanocomposites (WPNCs). The third section of the experimental work is the analytical testing which conducted to investigate the properties to ensure the WPNCs produced would be greatly enhanced. Both the raw and treated wood samples are synthesized in all experiments. To ensure the accuracy of the experimental work, a total of ten wood samples for each species are used in every treatment. This chapter also includes the materials as well as methods to fabricate WPNCs. Besides, all the characterizations involved throughout the whole book will be included in this chapter.

2 Methods Related for Wood Polymer Nanocomposites (WPNC)

2.1 Curing Methods for Wood Polymer Nanocomposites (WPNC) Preparation

With the various curing processes, it can well convert a monomer or a prepolymer that was used to impregnate in wood. All these techniques can be explained in detail.

The first technique is radiation curing. It is a very commercial production of wood polymer materials that began in the mid-1960s using the radiation process. There are few examples of this type of radiation which included atomic particles, neutrons, photons, gamma rays, X-rays, and electrons (Betty 1976; Dobрева et al. 2006). Gamma radiation treatment appears to be the cheapest and most practical due to the uniform distribution of the polymer within the sections of wood when gamma rays penetrate the wood. However, radiation curing had a main drawback which was the safety and environment concerns. In addition, the transportation of the various wood products to and from the irradiation site was prohibitive (Dobрева et al. 2006; Meyer et al. 1965). According to Meyer et al. 1965, catalyst-heat technique was another method to treat WPNCs.

When it reached the early of 1980s, the process of producing WPNCs using catalyst-heat process was much more widely used than radiation process throughout the USA. The specific catalyst-heat process which was the microwave heating curing was the most widely used. This process occurred when heat transfers from the surface into the materials especially for the wood. However, the heating rate of a

wood material was limited. Based on the researches carried out by Galperin et al. (1995) and Patyakin et al. (2008), microwave radiation had been found to be efficient for curing treatment of an impregnated wood. Urea and formaldehyde resin solutions were used to impregnate the wood species at various temperature which change the behavior of wood products (Galperin et al. 1995). This research showed that the birch samples used 150 s to heat up 100⁰ C for microwave treatment, while the same samples used 1920s to reach the same temperature for convective heating process.

2.2 Wood-Hardening Process

In the past research, many efforts had been carried out to improve wood properties physically or chemically. Therefore, there was a great establishment in knowledge and different techniques for wood quality improvement to ensure the modified wood products can be widely applied in different niches. The techniques that were commonly used for hardening wood included impregnation with reactive chemicals, compression, or combination of chemical impregnation and compression. The new WPNCs produced showed better dimensional stability, compressive strength, and hardness compared to the original wood (Bodirlau et al. 2009; Schneider 1994; Ayer et al. 2003; Devi et al. 2003).

The introduction of a monomer into the empty voids within the cell tissue will greatly improve the hardness of raw wood. The filling can be done by impregnating the liquid into the wood in a closed space. This can have caused wood hardening. One of the examples monomers used in the impregnation was the styrene or methyl methacrylate (MMA) that becomes solid by polymerization. However, this type of impregnation showed one major challenge which was the proper technique for well impregnation of the liquid monomer into the cell tissue of wood due to the poor permeability of most species of wood. Besides, wood would be burnt or split once the polymerization took place due to the impregnation process. To overcome this challenge, the liquid monomer should be well impregnated into the cell tissue of the wood through vacuum impregnation or pressure impregnation to ensure the poor permeability of wood was greatly enhanced.

In general, reactive monomers or prepolymers can be impregnated into the raw wood through suitable techniques such as heat impregnation with the proper polymer initiator. As mentioned previously, wood splitting or wood burning as well as the changes in the wood dimensions can be happened due to the exothermal polymerization reaction occurred with the cell tissue of the wood. These can be happened because the temperature within the wood rises to a very high level during the polymerization reactions. Therefore, suitable method such as the application of radiation can be carried out to initiate and control the polymerization reactions. For this case, raw wood can be treated by gamma radiation. The polymerization reaction impact on the anatomic structure, chemical structure, density, viscosity, composition of the wood cell wall whereas the polarity of the monomer that can affect the wood impregnation process.

2.3 Monomer and Polymer Treatments

The introduction of suitable liquid monomer or prepolymer into the cell lumens of wood to produce polymerized wood usually remains their original desirable characteristics with the addition of improved properties. Similar to the conventional wood-treated product, most of the wood species can be readily impregnated with various monomers or prepolymers through suitable equipment and techniques. For example, the impregnation of vinyl polymers into wood contributes better performance especially in preservation, mechanical properties, and the water repellency. This type of impregnation by using curing greatly improved the moisture resistance and hardness of wood (Bodirlau et al. 2009; Meyer et al. 1978). Besides, catalysts should be applied in the polymerization of vinyl monomer with wood (Bodirlau et al. 2009; Yan et al. 2009; Meyer et al. 1965; Inoue et al. 1993). In addition, radiation technique was used for vinyl monomer to impregnate the wood species. (Siau 1969; Yan et al. 2009). According to Langwig et al. (1968), wood can be polymerized by *t*-butyl styrene, epoxy monomers, and methyl methacrylate via in situ impregnation.

With the introduction of monomer into wood through impregnation, the properties of WPNCs such as hardness and static bending strength significantly increased. Through this, the wood can be effectively stabilized with the impregnation of vinyl polymer into the wood by bulking the cell wall (Timmons et al. 1971). However, vinyl monomers except for acrylonitrile are all poor swelling agents for wood (Bodirlau et al. 2009; Yan et al. 2009; Loos and Robinson 1968). Based on the research carried out by Ellwood et al. (1972), it was clearly mentioned that the dimensional stabilization of wood with vinyl monomers had been gradually increased. For wood impregnated with styrene, this WPNC has been largely investigated which significantly improved the water repellency, compression, and bending strength (Baki et al. 1993). Moreover, the research of Meyer et al. (1965) investigated that wood–styrene combinations through radiation techniques showed the well bulking of wood with styrene as well as the with gamma irradiation.

Besides mechanical properties, the dimensional stability of wood was improved. However, an initial swelling of wood by water or some other polar solvent was required. There are two different types of impregnation, namely solvent exchange and high-vacuum methods. Besides, gamma irradiation impregnation wood showed better properties such as improving dimensional stability and tangential tensile strength. In addition, modulus of rupture and modulus of elasticity were improved through the gamma radiation impregnation. Based on the previous research by Bodirlau et al. (2009), the styrene/glycidyl methacrylate (GMA) WPNCs showed higher anti-shrink efficiency value with value 53%, while styrene-treated wood samples showed 23% anti-shrink efficiency value for 24 h in water. However, both styrene/GMA WPNCs and styrene-treated wood samples showed similar hardness with an increment by 33% compared to raw wood samples.

To synthesize WPNCs, methyl methacrylate (MMA) is another type of vinyl monomers. MMA is commonly used because it is an inexpensive, clear-colored, and commodity chemical. MMA is one of the most widely used monomers in

making clear and colored WPNCs (Duran and Meyer 1972; Langwing et al. 1968, 1969; Noah and Foudjet 1988; Siau and Meyer 1966; Siau et al. 1968, 1978; Yalinkilic et al. 1998; Yan et al. 2009). According to Loos and Robinson (1968) and Yan et al. (2009), the wood swelled with the addition of MMA that led to a small change in dimensional stability. However, the cell walls remained unchanged for MMA-treated wood. MMA-treated WPNCs were time-dependent dimensional stability improvement which defined that these WPNCs would degrade over the years until the end; these WPNCs showed almost the similar properties as raw wood.

The properties of WPNCs produced are usually characterized through compression parallel to grain direction, static bending strength, dynamic modulus of elasticity, and dielectric constant. The mentioned properties are investigated through different theoretical equations which derived from an assumed cellular model. These theoretical equations can be used as a reference for the experimental works for the WPNCs formed. For raw wood, it was found that the hardness of wood was closely related to the density of raw wood. On the other hand, the hardness of the treated wood was more related to the hardness modulus, density, and polymer loading. From the impregnation or treatment, the impregnated or treated wood with methacrylate polymers showed better properties including the decrement in the rate of moisture uptake, higher mechanical properties such as modulus of elasticity and rupture, higher fiber stress at proportional limit, improved maximum load, and crushing strength limits as well as greater hardness index compared to the raw wood (Ates et al. 2009; Langwig et al. 1968; Rowell et al. 1982).

From the research carried out by Juneja and Hodgins (1970), it studied on the impregnation as well as the polymerization of vinyl chloride with different conditions in the raw wood. As the polymerization reaction was highly exothermic, the WPNCs produced were distorted and discolored. The discoloration of WPNCs occurred due to the conjugated double bonds left along the chain when the hydrogen chloride was released during the degradation of the polyvinyl chloride (PVC). Therefore, vinyl chloride was not a suitable monomer for producing WPNCs due to three reasons. First, the mechanical properties of PVC-related WPNCs were only slightly improved. Second is that the discoloration and deformation happened as the heat of reaction was higher. The third reason is that the insoluble polyvinyl chloride formed fine powder precipitate during the reaction. The fine powder would not improve the mechanical properties of the PVC-related WPNCs formed.

The method to develop WPNCs is important. WPNCs can be synthesized through in situ polymerization of ethyl α -hydroxymethylacrylates (EHMA) (Mathias and Wright 1989). EHMA is a good monomer to be impregnated into WPNCs. The monomer as reported can penetrate the cell walls of the wood fibers which formed a complete WPNC. Bryant (1966) investigated that the mechanical properties of phenolic resin-impregnated wood were greatly increased. Besides, he

also investigated the changes in relative molecular size as well as the concentration of phenolic resin on dimensional stabilization of WPNCs. Water-soluble phenolic resins are usually used to impregnate wood by bulking the cell wall structure and at the same time preventing shrinkage of wood upon drying. However, the application of phenolic resin-modified wood products is limited due to their dark brown color on the surface of the products.

To ensure the improvement in modulus of elasticity, modulus of rupture, and higher thickness swelling, the compression of boards should be significantly increased. Besides phenolic resin mentioned above, aqueous polyurethane emulsion can be introduced into raw wood as it consists of low molecular weight components in aqueous media (Hartman 1969). This aqueous polyurethane system could be reused without affecting the polymerization at room temperature. It was clearly proven that better diffusion and penetration could be obtained with the impregnation of lower molecular weight resin (Yan et al. 2009). Apart from polyurethane, amino resin formed by melamine (1, 3, 5-triamino-2, 4, 6-triazine) and formaldehyde has been commercially used for over 60 years. Another polymer named melamine formaldehyde (MF) is one of the hardest and stiffest isotropic polymeric materials with low flammability. This type of polymeric material is applied in decorative laminates, molding compounds, adhesives, coatings, and other products. These advantageous properties helped to improve properties of raw wood such as surface hardness and modulus of elasticity (MOE) (Ates et al. 2009; Deka and Saikia 2000; Georgieva et al. 2008; Mirov et al. 1995).

In addition, poly(ethylene glycols) (PEG) can be widely used in the field of the dimensional stabilization of wet wood (Georgieva et al. 2008; Hoffmann 1988, 1990; Stamm 1959, 1964a, b). PEG is a water-soluble synthetic wax. The addition of heated PEG into the raw wood increased the strength by replacing the hydroxyl group within the raw wood with PEG. Not only PEG, alkylene oxide is another specific polymer that can be introduced into the raw wood. Based on the previous research, the impregnation of alkylene oxide may improve the dimensional stability of wood due to the changes in hydrophilic nature of wood (Ates et al. 2009; Georgieva et al. 2008; Guevara and Moslemi 1984; Rowell 1975; Rowell et al. 1976). WPNCs prepared by Rowell et al. (1982) were formed through the combination treatment of cell wall grafting with alkylene oxides and lumen treatments with methyl methacrylate.

WPNCs that were prepared using a two-stage treatment resulted a higher stabilized WPNCs. The first-stage treatment is that raw wood chemically modified the cell walls of southern pine and sugar maple with propylene oxide. Propylene oxide in this case was functioned to reduce the flexural strength of the wood. For second-stage treatment, methyl methacrylate (MMA) was impregnated into the void volumes of raw wood. Another research on the combination of wood with alkoxysilane was carried out by Su and Wilkie (2003). Alkoxysilane was used as coupling agent that helped to increase the chemical impregnation reaction within the raw wood tissue.

2.4 Other Treatments

Due to the advanced technology, wood inorganic nanocomposites can be fabricated through the introduction of inorganic substances into the wood's cell walls (Furuno et al. 1991, 1992a, b; Ogiso and Saka 1993; Saka et al. 1992; Saka and Yakake 1993; Tunc et al. 2010; Yamaguchi 1994a, b; Yan et al. 2009; Zollfrank and Wegener 2002). Wood inorganic nanocomposites were synthesized to improve the fire and decay resistance properties. For example, a combination of acetylated and propionylated formed wood silicate nanocomposites (Li et al. 2001). Besides, wood silicate nanocomposites could also be impregnated with an aqueous sodium silicate solution that improved the dimensional stability. The filler such as silicate gels were incorporated in WPNCs which enhanced the flame-resistance as it helped to increase the oxygen index of the WPNCs.

2.5 Combination of Two or Three Monomers

WPNCs can be produced with one or more monomers. From the researcher carried out by the cell wall and cell lumen of WPNCs were investigated. Both furfuryl alcohol-based (FA) cell wall and methyl methacrylate-based (MMA) combination formulations were introduced into the raw wood. Besides, the wood cell wall could be modified with acetic anhydride, while lumen could be filled with methyl methacrylate (MMA). Their effectiveness in reducing the rate of moisture sorption and degradative effects of accelerated weathering was investigated by Feist et al. (1991). This showed the effectiveness in reducing the rate of swelling and reducing erosion up to 85% due to accelerated weathering through the combined treatment of acetylation followed by methacrylate impregnation. On the other hand, cell lumens could be fully filled with bioactive polymer. However, this polymer might lead to solubility and penetration problem as the polymers had low solubility but high viscosity. Therefore, bioactive group polymer should be used together with a monomer to fill the wood. Besides, the combination of bioactive polymer with monomer should be carried out through in situ polymerization or copolymerization with the aid of a catalyst that led to higher loading of the bioactive polymer into the wood.

2.6 Chemical Impregnation and Compression of Wood

Chemical impregnation is one of the common methods to harden the raw wood for value-added applications. In year 1940s, compressed (compreg) high-density wood for manufacturing airplane propellers was produced with the impregnation of

phenol formaldehyde (PF). Recently, the impregnated wood polymer nanocomposites are widely used in the industrial applications such as bolts, rivets, gears, high and low tension circuit breakers, turbo generators, sports goods and chair seats etc.

2.7 Summary of Wood Quality Improvement Methods and Technologies

Although wood is a common material to be applied in industrial application, it consists of some drawbacks that include high moisture uptake, biodegradation, and dimensional variations. All these drawbacks happened due to the presence of numerous hydroxyl groups within the raw wood components and different cavities in the wood. Due to this drawback, raw wood is necessary to be modified. There are some techniques that can be well applied in modifying wood, namely impregnation with reactive chemicals, compression, and the combination method of chemical impregnation and compression. Different techniques of wood modification were carried out to improve the properties of wood. Recently, chemical modification on wood is increasing due to the great improvement in the hardness, mechanical properties, and dimensional stability of WPNCs formed. Two major types of polymer which are thermoplastic and thermosetting systems have been used in the impregnation of raw wood through in situ polymerization of monomers such as styrene and methyl methacrylate, or prepolymers such as phenol formaldehyde as these methods are the most common and inexpensive technique. In the early 1960, chemical modification was widely performed to obtain better properties of WPNCs. As mentioned previously, vinyl monomers do not strongly bond with the component and thus, the monomers usually filled only the empty lumens of the wood. With the filling of monomer into lumens, the dimensional stability of WPNC can be greatly improved. On the other hand, the introduction of polar monomers led to better chemical resistance as well as dimensional stability of WPNCs.

To ensure the vinyl monomer can be applied in chemical modification, vinyl monomer itself should be modified by introduction of polar groups such as ethyl α -hydroxymethylacrylate (HMA). HMA is recognized to be good monomer for cell wall swelling. However, the monomer modification is a time-consuming process. Thermosetting resin such as water-soluble phenolic resins, urea formaldehyde, and melamine-formaldehyde prepolymers was all suitable to be applied in improving its compressive strength properties and at the same time reduced shrinking and swelling behaviors. These resins penetrated and bulked the cell wall to react with the hydroxyl groups of the raw wood. This caused the brittleness and toughness properties of the raw wood to deteriorate.

3 Methods

Solid wood is one of the most important structural and renewable raw materials that are abundantly available in the world. Natural beauty, durability, and versatility make wood the preferred material for many uses. Nevertheless, wood has a few drawbacks which limit its use, including high moisture uptake, biodegradation, and physico-mechanical properties which change with environmental variation (Vetter et al. 2009; Yalinkilic et al. 1998). Recently, raw wood is modified intensively through in situ reinforcement with the addition of silicate and nanoclays (Cai et al. 2007a, b, 2008). Besides, suitable treatment improved the physical and morphological properties of WPNCs (Bergman et al. 2009; Islam et al. 2011; Yildiz et al. 2005). Thermal and mechanical properties of wood could improve when treated with chemical treatment (Larsson and Simonson 1994). To ensure the properties could be improved, different kinds of chemicals, namely styrene, methyl methacrylate, sodium metaperiodate, phenyl hydrazine, *N, N*-dimethylacetamid, phenol-formaldehyde resin, maleic acid, ethylene glycol dimethacrylate, 3-(trimethoxysilyl)propyl methacrylate, acrylonitrile, butyl methacrylate, furfuryl alcohol, ethyl methacrylate, glycidyl methacrylate, and urea formaldehyde, have been extensively used in impregnation of raw wood. This was due to the addition of these chemicals improved the wood properties. However, some chemicals had their own limitations (Islam et al. 2010; Rowell 2005).

In the recent years, there are many researches on the improvement of properties of wood which was modified by nanotechnological modification effectively (Cai et al. 2007a, b, 2008). According to Border et al. (2009), the incorporation of different layered silicates and nanoclay (montmorillonite, hectorite and saponite) incorporate into the composites which led the composites to a higher stiffness and strength. With nanotechnological modification, WPNCs with organophilic-layered silicate via in situ nanoreinforcement improved the wood properties. Moreover, lower silicate loading thermoplastic and thermoset nanocomposites considerable improvements in physical properties, mechanical properties which included tensile modulus and strength, flexural modulus and strength, thermal properties such as thermal stability, flame retardant as well as barrier resistance (Ray and Okamoto 2003). Due to the advantageous properties, the nanotechnological technique is perceived as potential in improving the properties of solid wood to obtain better products.

Tropical light hardwood is abundantly available in quantity. However, their quality of raw wood is poor to be utilized on specific purposes due to their poor physico-mechanical and thermal properties. Suitable chemical modification is required before they can be utilized. The discussed newly developed nanotechnological modification technique on selected tropical woods can be promising for this approach. However, there is less research that has been carried out on the nanotechnological modifications. In addition, less research has been carried out on the chemical modification of Malaysian tropical light hardwood species especially with nanoclay and chemicals combination technique.

One of the characterizations that are used to study the effect of temperature on thermomechanical properties of WPNCs is dynamic mechanical thermal analysis (DMTA) (Luckenbach, Rheometrics Inc. (Sealsestem 1994)). DMTA managed to determine the viscoelastic behavior of WPNCs, and at the same time, it provided important information on the structure, morphology, and properties of WPNCs (Mancado and Arroyo 2000). According to Salmen (1984), the viscoelastic behavior of wood greatly depended on the response of the cellular structure to mechanical force. The temperature-dependent dynamic parameters such as dynamic modulus, storage modulus, and loss modulus are classified as temperature-dependent dynamic parameters, and mechanical damping ($\tan \delta$) is used to investigate the interface and interaction between the layered silicate or nanoclay on the polymer matrix. There are many researchers proved that WPNCs showed better thermomechanical properties through DMTA analysis (Hamdan et al. 2010; Sugijama et al. 1996).

Besides, free-free flexural vibration method is another method specifically used to investigate the dynamic Young's modulus of wood. According to Halabe et al. (1995), free-free vibration method is one of the nondestructive testing (NDT) methods that are widely applied in timber industry which are used to measure the elastic properties and energy dissipation of raw wood and WPNCs (Halabe et al. 1995). This testing provided accurate information on the stiffness of the WPNCs. Besides, three types of vibration, which are bending (flexural), longitudinal (axial), and torsion, are well determined by the nature of vibration. From the three mentioned vibration methods, the flexural vibration method is the most widely used method as it is easier to excite and detect the vibrations under investigation.

In this research, different types of tropical wood species were selected and fabricated with the aid of phenol-formaldehyde resin (PF) and halloysite nanoclay. All the prepolymer mixture was impregnated into the raw tropical wood by vacuum-pressure method and in situ polymerization. Based on the previous research, it was clearly shown properties of WPNCs formed affected the percentage of weight gain and the density. Nanoclay was incorporated into the wood, and this was confirmed through the characterization such as FTIR and SEM, respectively. Besides, mechanical properties of WPNCs especially the modulus of elasticity (MOE) and compressive modulus could be improved significantly. Dynamic mechanical thermal analysis (DMTA) was used to investigate the thermomechanical properties of raw wood and WPNCs over the temperature -100 to 200 °C. DMTA was also used to evaluate the intrinsic properties of the components, morphology of the system, and the nature of interface between the phases. In addition, the storage modulus (E') of both raw wood and WPNCs was investigated to determine the improvement in both glassy region and rubbery plateau over the temperature range. Furthermore, WPNCs were improved especially on the surface interphase through the investigation on the damping peaks ($\tan \delta$) which lowered after the modification or treatment. Dynamic Young's modulus (E_d) of wood was calculated using free-free vibration testing which proved the significant

improvement on the impregnated WPNCs. Moreover, decay resistance of both raw wood and WPNCs was investigated through fungi test. All the wood samples were exposed to two types of fungi, namely white rot (*polyporus versicolor*) and brown rot (*postia placenta*), for 12 weeks, and the weight loss was presented in percentage (%) form. From this characterization, WPNCs showed higher decay resistance compared to raw wood.

3.1 Flowchart of Project

This project started with the title received from the department. Once the title was received, more research on the information about wood was carried out, followed by the identification of problem statement and objectives of the project. After clearly finalized the problem statement and objectives, the literature review study especially on mechanical properties, the pros and cons of raw wood and fabricated WPNCs as well as the method of wood modifications was carried out. Continuously, the experiment was investigated based on the research and was carried out consecutively. After carrying out laboratory work, the results obtained would be analyzed and discussed. Lastly, conclusion would be made to summarize the experimental results together with analysis and explanation of the project. Figure 1 showed the flowchart of project as the reference of this project to ensure the project went smoothly.

3.2 Preparation of WPNCs

The process to fabricate WPNC is shown in Fig. 2. All the samples were oven dried to constant weight at 105 °C before treatment. All the dimensions and weights before and after treatment were measured, respectively. The samples were then placed in an impregnation vacuum chamber to synthesize WPNCs. All the samples were undergoing vacuum chamber with pressure of 10 kPa for 30 min to remove air from the pores of the samples formed. An accurate amount of monomers and initiator was introduced into the chamber until the samples were completely covered. The samples were kept immersed in the monomer solution for 6 h. Besides, all the samples were ensured to be placed at ambient temperature and atmospheric pressure to obtain further impregnation. Continuously, the samples were removed from the chamber and all the excess chemicals were wiped off from wood surfaces. Lastly, the samples were wrapped with aluminum foil and placed in an oven for 24 h at 105 °C for polymerization to take place (Deka and Saikia 2000; Devi et al. 2003). All the polymerized samples formed were weighted to determine weight percentage gain (WPG).

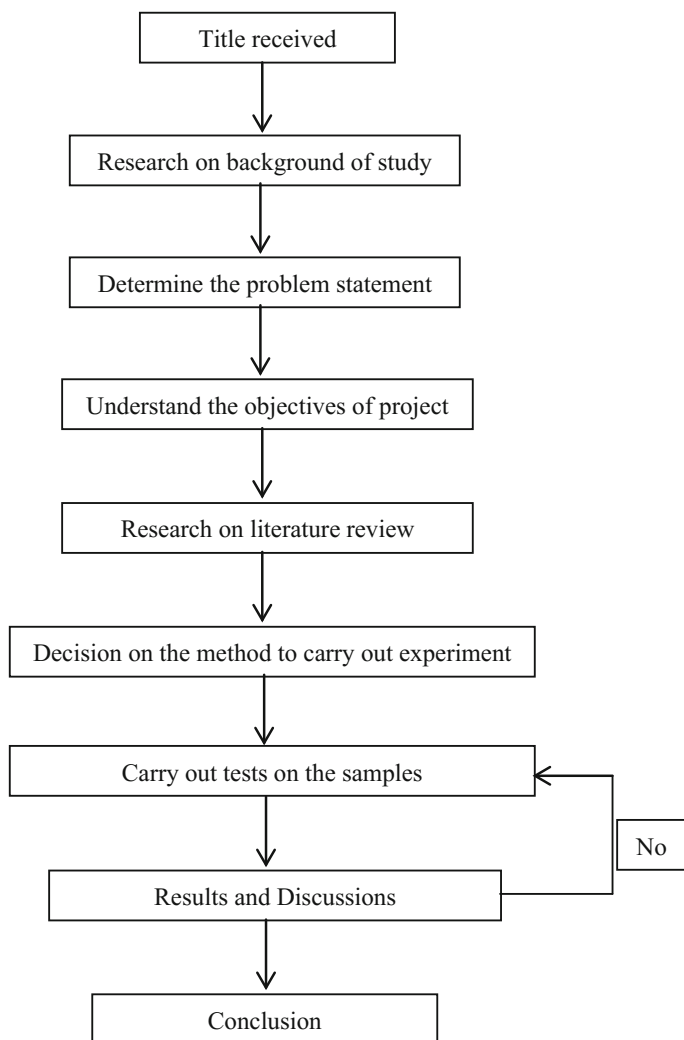


Fig. 1 Flowchart of project

3.3 Characterization of Wood Polymer Nanocomposites (WPNC)

3.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

One of the common analytical characterizations that have been applied in pharmaceutical, life sciences, and electronic industries is Fourier Transform Infrared Spectroscopy (FT-IR). This characterization included structural information of

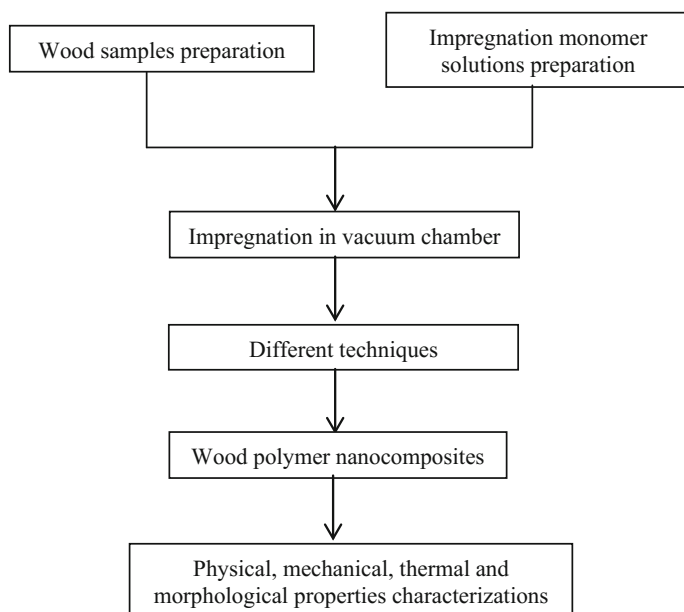


Fig. 2 Schematic diagram of the experimental procedure

Table 1 Functional groups with band position (FlashcardExchange.com, 2012)

Functional groups	Band position (cm^{-1})	Intensity
C–H (alkyl group)	2850–2960	Medium to strong
=C–H (alkene)	3020–3100	Medium
C=C	1650–1670	Medium
$\equiv\text{C}-\text{H}$	3300	Strong
$\text{C}\equiv\text{C}$	2100–2260	Medium
C–Cl	600–800	Strong
C–Br	500–600	Strong
C–I	500	Strong
O–H	3300–3540	Strong, broad
C–O	1050–1150	Strong
Aromatic ring	1600, 1500	Strong
N–H	3310–3500	Medium
C–N	1030, 1230	Medium
C=O	1670–1780	Strong
O–H (carboxylic acid)	2500–3100	Strong, very broad
$\text{C}\equiv\text{N}$	2210–2260	Medium

materials, analysis of materials as well as determination of contaminations IR Absorptions of Functional Groups (FlashcardExchange, United States of America 2006). The functional groups with its band position were shown in Table 1 (FlashcardExchange.com 2012). This equipment was used to determine the chemical change upon impregnation of the raw wood with impregnation of chemicals.

From Fig. 3, it showed FT-IR-branded Shimadzu IRAffinity-1 that was well applied with the guidance of operators. This FT-IR machine was kept in a clean and safe place to prevent any damage on it. Besides, chemical such as ethanol was used to remove stains and microorganisms. Both raw wood and WPNCs powders were taken out from the plastic tube using spatula and placed on top of the specimen in the FT-IR machine. The knob in the FT-IR machine was tightened. Continuously, the button “sample” appeared in the computer connected was then pressed. After 3 min, all the peaks in the graph form were shown. All the steps were repeated for all the raw wood and WPNCs samples. The infrared spectra of raw wood and WPNCs were recorded on a Shimadzu IRAffinity-1 at 20 scans with a resolution of 4 cm^{-1} . The intensity range used for this test is from 4000 to 600 cm^{-1} .

Fig. 3 FT-IR machine



3.3.2 Compression Test

Compression test can be carried out to determine the mechanical properties of both raw wood and WPNCs. Mechanical properties, namely modulus of rupture (MOR) and modulus of elasticity (MOE), could be tested through compression machine branded Shimadzu Universal Testing Machine. This machine functioned according to ASTM D-143 (1996) as shown in Fig. 4. It has the maximum loading capacity of 300kN with the crosshead speed of 10 mm/min. All the fabricated samples were stored at 85 °C inside a cool incubator for four days.

This test was carried out to ensure all the fabricated WPNCs withstand higher force compared to raw wood. For each experiment, 20 samples were prepared to undergo compression test. To obtain the result, the machine is well linked to the computer and all the compression test can be carried out using software named Trapezium2. The software Trapezium2 can be consistently applied as shown in Table 2 as well as in Figs. 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, and 19.

Fig. 4 Compression machine



Table 2 Thirteen steps used in compression testing software

Steps	Explanation
1	The overview of software
2	The icon “New” was clicked and followed by the clicking on “Method”
3	A command box was shown. The icon “No” should be clicked
4	Method Wizard will appear. The “Next” icon should be clicked
5	Icon “Comp.” should be clicked, and “Next” icon was clicked after that
6	The “Next” icon should be clicked
7	V1’s value was changed depending on the requirement, and “Next” icon was clicked
8	The value of wood sample’s dimensions was changed and click “Next” icon
9	There are three figures that did not change by just clicking “Next”
10	Method Wizard completed by clicking the “Finish” icon
11	The position and force value should reset it at zero
12	A Navigation Bar was shown and click “Start” icon
13	Begin Test is pressed and navigation bar will show a “Stop” icon

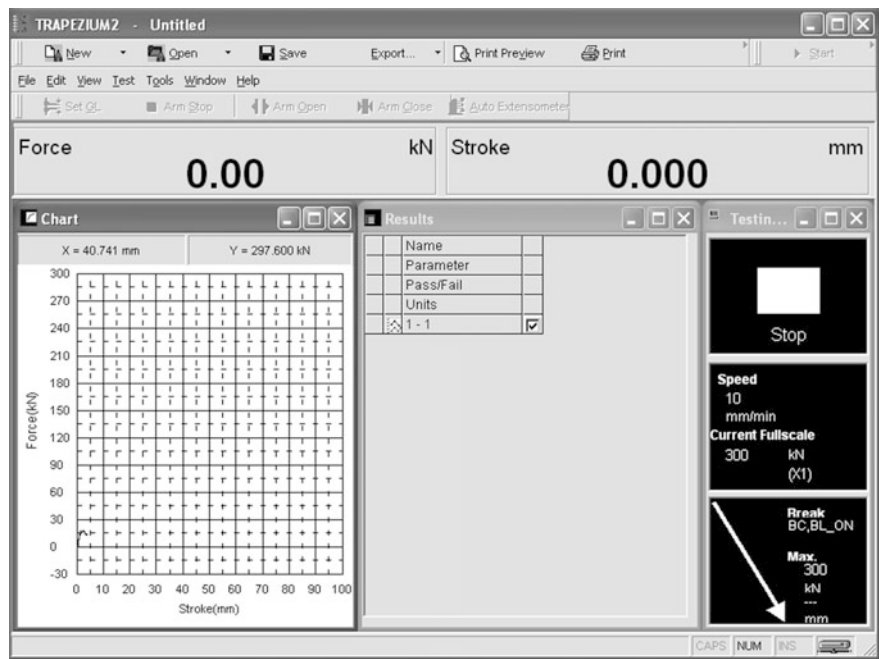


Fig. 5 Software overview

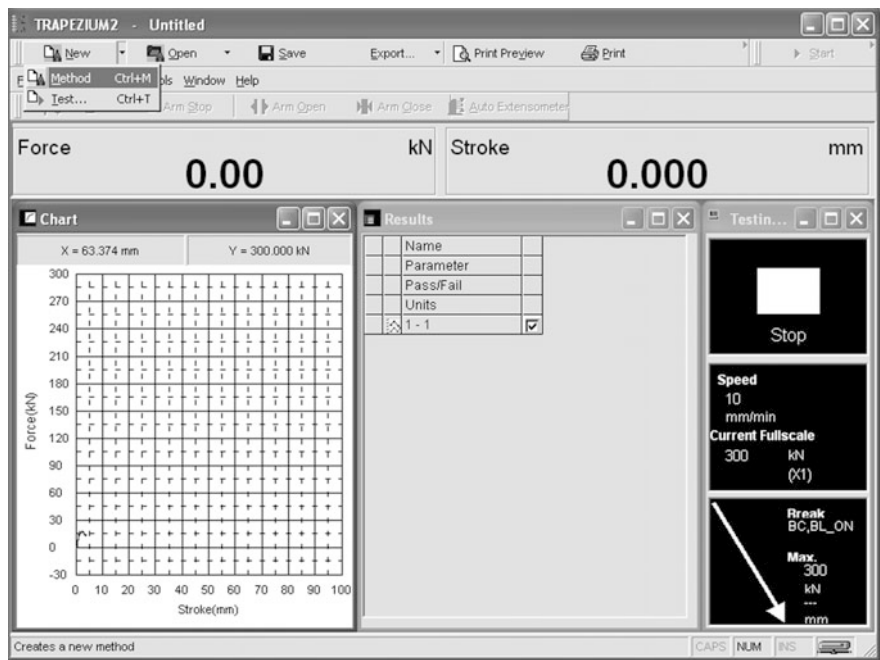
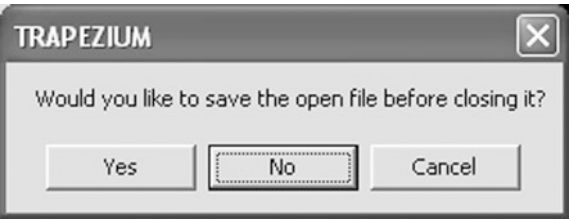


Fig. 6 Second step’s overview

Fig. 7 Third step’s overview



3.3.3 Thermogravimetric Analysis (TGA)

For thermal properties, Thermogravimetric Analysis (TGA) is carried out. This characterization is used to determine the degradation temperatures or absorbed moisture content of materials especially on polymer nanocomposites. TGA is a process which can determine the percent by mass ratio of a solute through heat and stoichiometry ratios. The process involved heating a mixture to a high enough temperature to decompose the samples into a gas, which dissociated into the air. It was plotting weight percentage against temperature. TGA was used to investigate the corrosion kinetics in high-temperature oxidation.

TGA started with the weighing of a finely ground sample. The samples were then exposed to a heated chamber in the presence of oxygen. The weight losses of



Fig. 8 Fourth step's overview

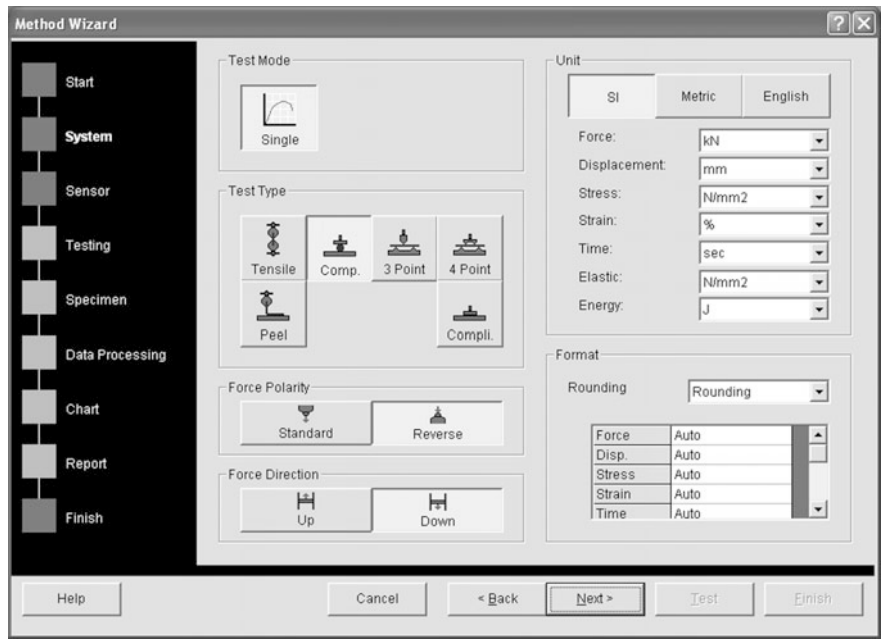
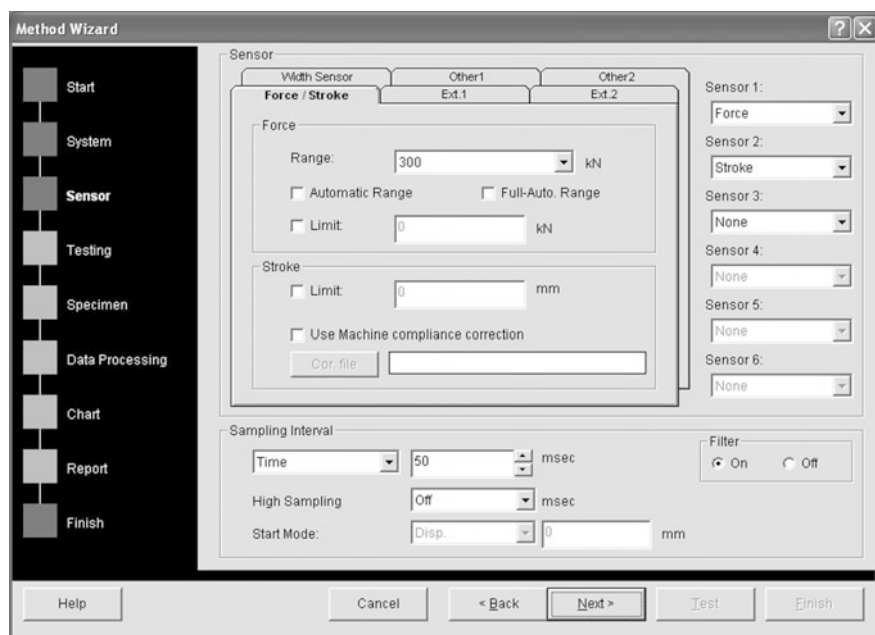


Fig. 9 Fifth step's overview



Method Wizard

Start System **Sensor** Testing Specimen Data Processing Chart Report Finish

Sensor

Width Sensor Other1 Other2
Force / Stroke Ext.1 Ext.2

Force

Range: 300 kN

☐ Automatic Range ☐ Full-Auto. Range

☐ Limit: 0 kN

Stroke

☐ Limit: 0 mm

☐ Use Machine compliance correction

Cor. file

Sensor 1: Force
Sensor 2: Stroke
Sensor 3: None
Sensor 4: None
Sensor 5: None
Sensor 6: None

Sampling Interval

Time 50 msec

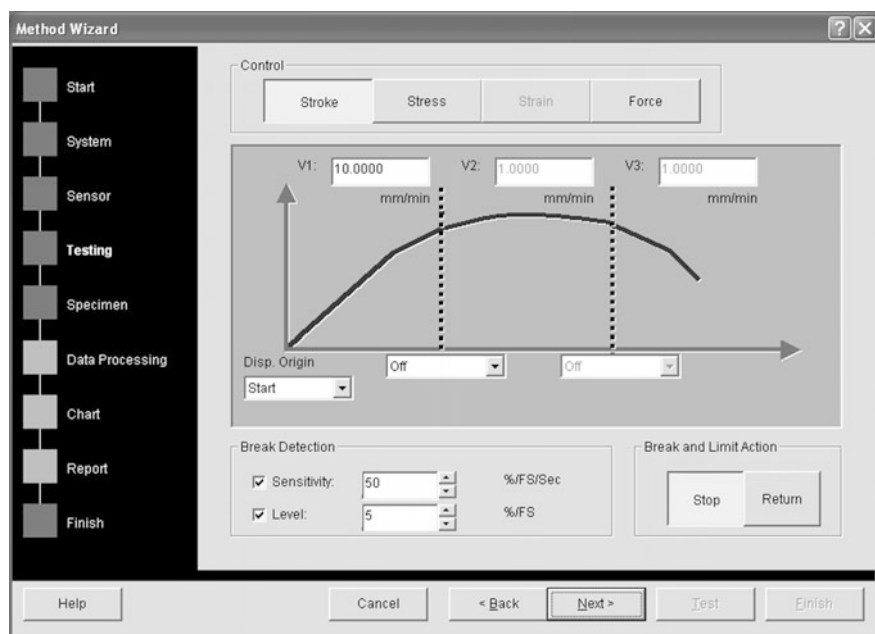
High Sampling Off msec

Start Mode: Disp. 0 mm

Filter ☒ On ☐ Off

Help Cancel < Back Next > Test Finish

Fig. 10 Sixth step's overview



Method Wizard

Start System Sensor Testing **Specimen** Data Processing Chart Report Finish

Control

Stroke Stress Strain Force

V1: 10.0000 mm/min V2: 1.0000 mm/min V3: 1.0000 mm/min

Disp. Origin Off Off

Start

Break Detection

☒ Sensitivity: 50 %FS/Sec

☒ Level: 5 %FS

Break and Limit Action

Stop Return

Help Cancel < Back Next > Test Finish

Fig. 11 Seventh step's overview

Method Wizard

Shape:

Material:

Size Unit:

Batch Size:

SubBatch Size:

☐ GL Correction

Size:

Specimen N	Thickness	Width	Height
1 - 1	20.0000	20.0000	60.0000

Constants:

1 - 1

Help Cancel < Back Next > Test Finish

Fig. 12 Eighth step's overview

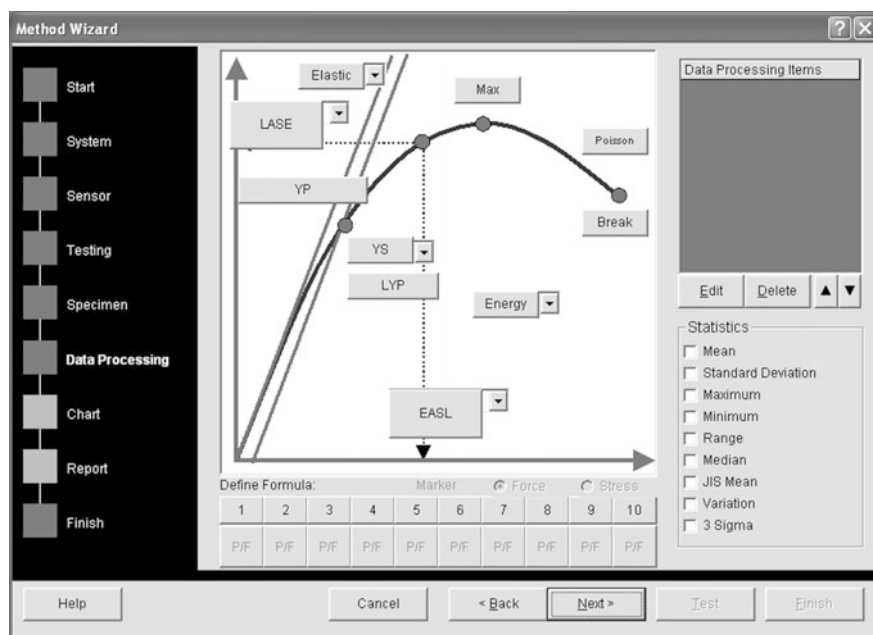


Fig. 13 Ninth step part 1's overview

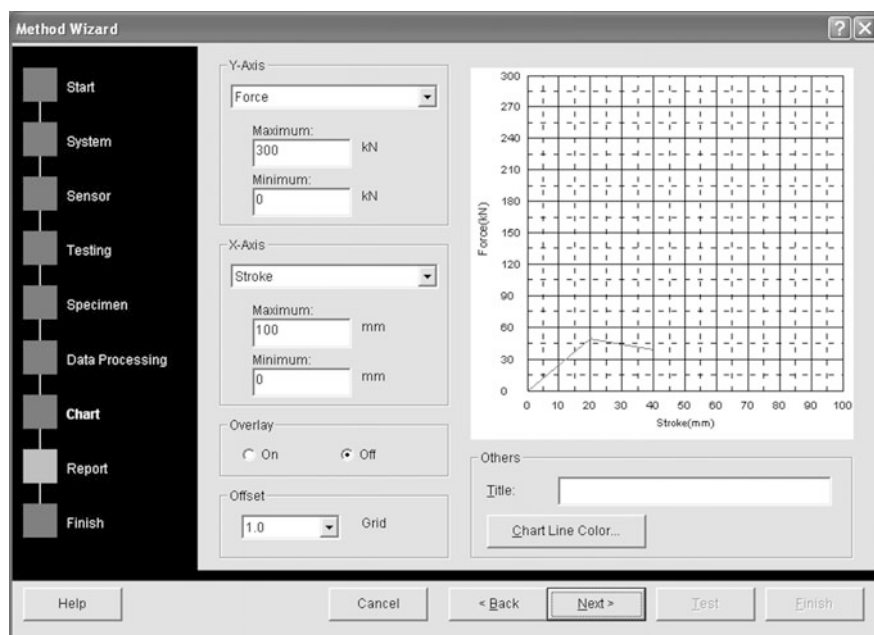


Fig. 14 Ninth step part 2's overview

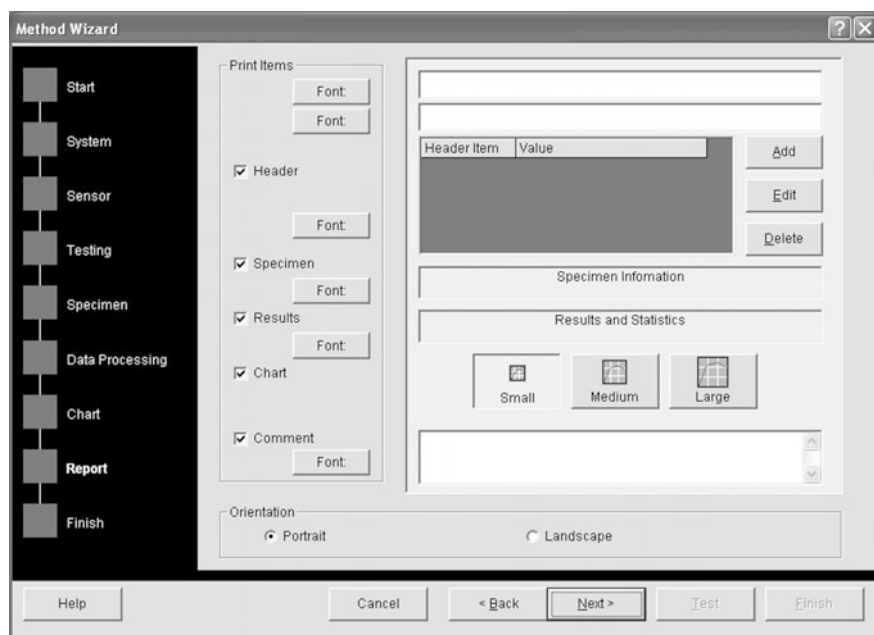


Fig. 15 Ninth step part 3's overview

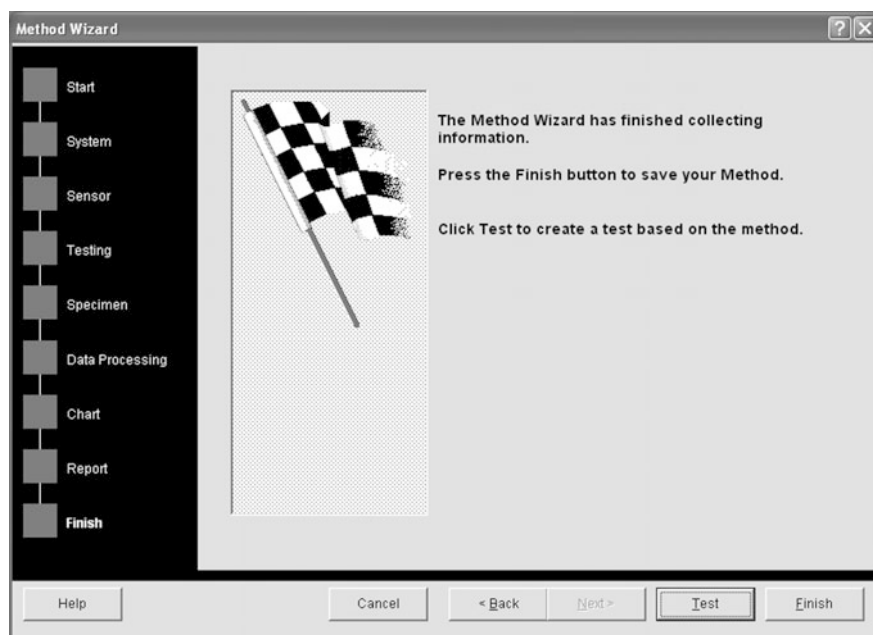


Fig. 16 Tenth step's overview

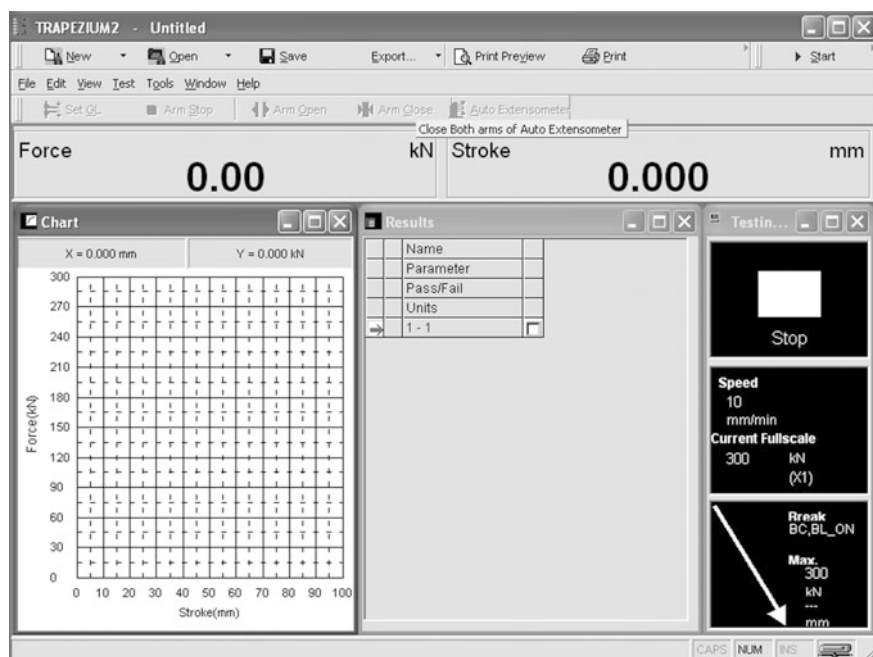
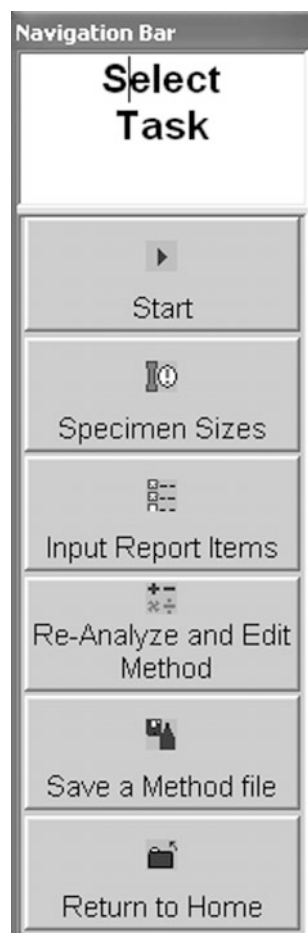


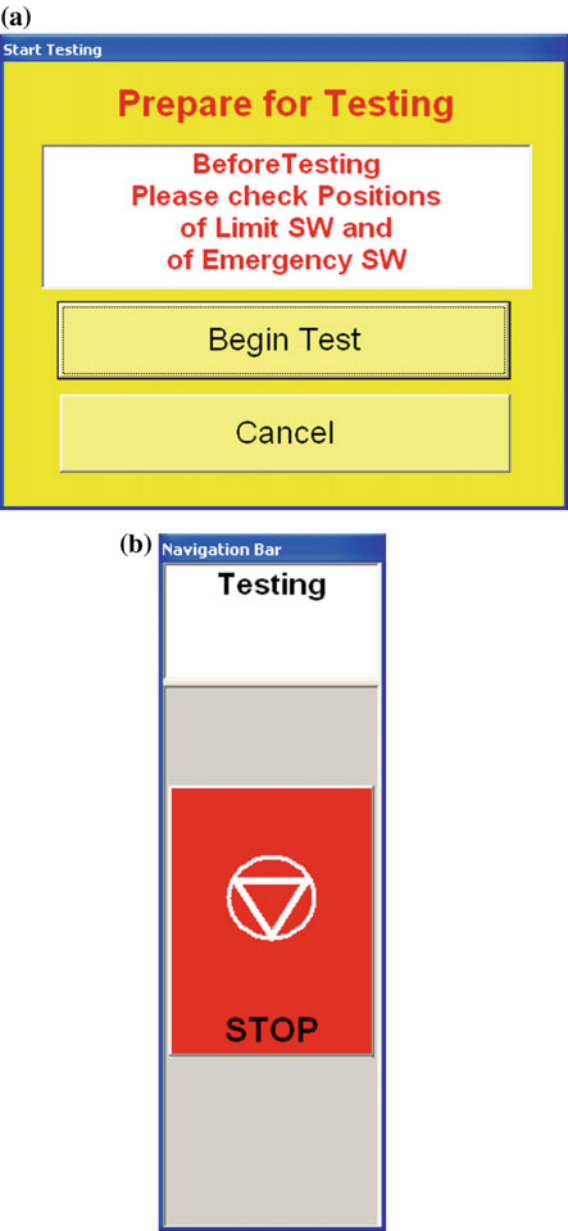
Fig. 17 Eleventh step's overview

Fig. 18 Navigation bar for starting



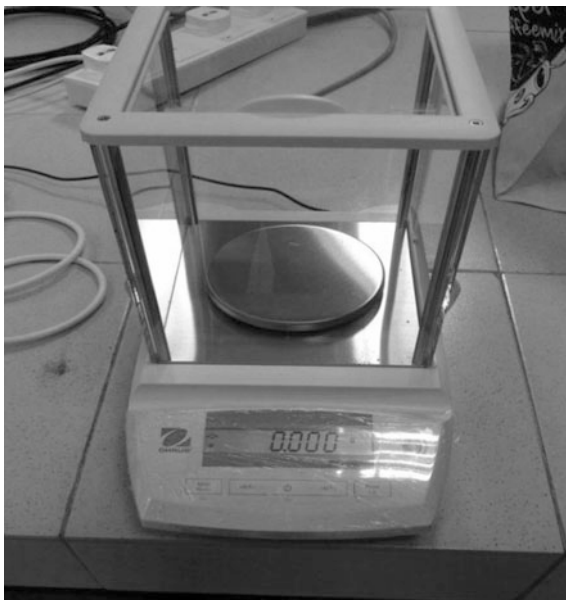
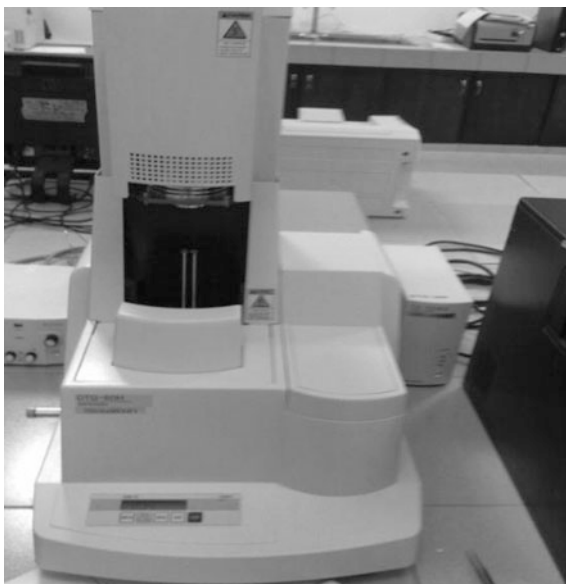
the samples were measured before the samples were heated. The change in weight of the sample was recorded as a function of time with temperature ranging from 20 to 700 °C. The rate of weight loss as a function of time and temperature could be measured after setting up. The use of a derivative computer was needed to record the results. After the data were obtained, curve smoothing and other operations could be carried out to find the exact points of inflection. In this method, temperature increased which led to increased weight loss. This was to investigate the exact temperature where a peak occurred more accurately. The weight for wood powders was measured using electronic balance as shown in Fig. 20. DTG-60H branded Shimadzu was used to run this testing as shown in Fig. 21.

Fig. 19 Begin test command and navigation bar for stopping



3.3.4 Scanning Electron Microscopy (SEM)

Besides FT-IR, compression test, and TGA, Scanning Electron Microscopy (SEM) was used to detect the pore size of the raw wood and WPNCs using

Fig. 20 Electronic balance**Fig. 21** DTG-60H

Scanning Electron Microscope under the warranty of Kosijaya Didactic Sdn. Bhd as shown in Fig. 22. The primary electron beam was produced by heating a metallic element under high vacuum at the top of the microscope. It was scanned across the surface of a specimen. The signal was generated when the electrons strike the



Fig. 22 Scanning electron microscope



Fig. 23 Coating machine

specimen. This was to detect the specific signals that produced an image of the surface. Three different types of signals that provided the greatest amount of information in SEM were the secondary electrons, backscattered electrons, and X-rays (Islam et al. 2011).

SEM was generally used to investigate the interfacial bonding between the cell wall polymer and reacted chemical. The specimens were first fixed with Karnovsky's fixative. It was then taken through a graded alcohol dehydration series. After the samples were dehydrated, all the samples undergo coating by a thin layer

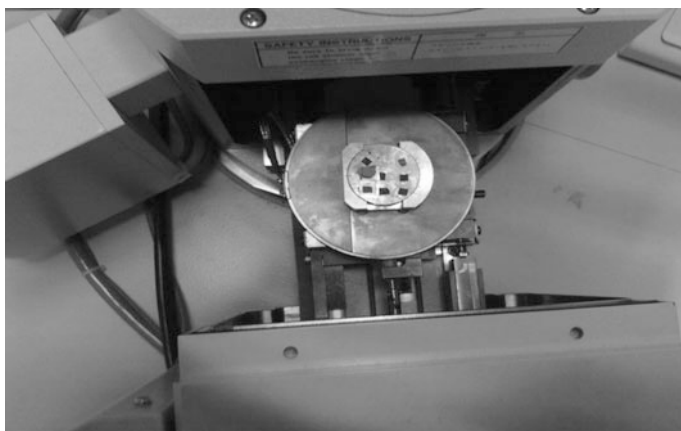


Fig. 24 Samples on top of the magnetic substance



Fig. 25 Picture shown by SEM-linked computer

of gold before viewing on the SEM. The micrographs were taken at magnification between $500\times$ and $1500\times$.

All the wood samples either in powder or solid form will be heated at temperature of 105°C for an hour before SEM test. This step was to remove moisture content of wood. For solid wood samples, $3\text{ cm} \times 3\text{ cm} \times 1\text{ cm}$ of raw wood and WPNCs were prepared.

After heating, both raw wood and WPNCs either in powder form or solid form would be coated. Before coating, the carbon tape was placed on top of the aluminum plate and the sample powders were placed on top of the carbon tape as

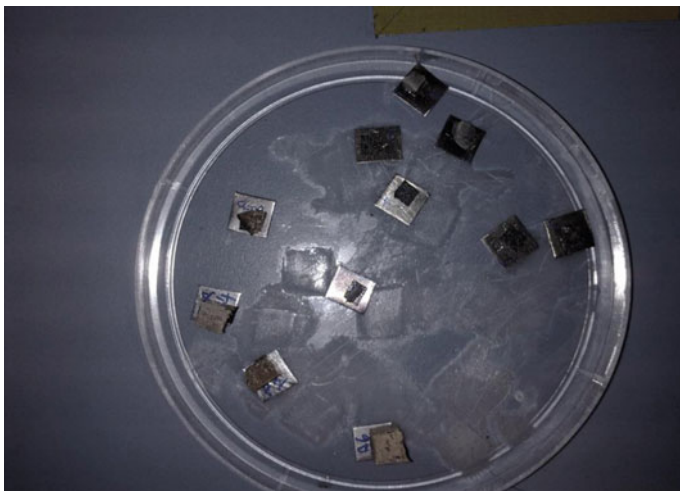


Fig. 26 Collected samples (powder and solid form)

shown in Fig. 23 for 15 min. The aluminum plate was placed aside to prevent the tested samples mixed with non-tested samples. A pair of forceps was used to clip the aluminum plate into the sampling tube.

Scanning electron process could be started after coating process. There were five samples placed on top of a magnetic substance with double tape to ensure the aluminum plate samples did not move randomly as shown in Fig. 24. After the machine start-up, the electron laser beam started to scan the samples (powder or solid form) by manual for this experiment. The picture scanned would be shown in computer linked as shown in Fig. 25, and the images would be saved into a folder. This step was repeated until all the samples were scanned. After the experiment was done, the samples were collected in a clean plate as shown in Fig. 26.

4 Summary

This chapter covered the overview, methods related to WPNCs, methods such as flowchart of project, preparation of WPNCs as well as characterization included Fourier Transform Infrared Spectroscopy (FT-IR), compression machine, Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM) in general.

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