DYNAMIC YOUNG'S MODULUS MEASUREMENT OF TREATED AND POST-TREATED TROPICAL WOOD POLYMER COMPOSITES (WPC)

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By means of dynamic mechanical thermal analysis (DMTA), selected tropical wood species, namely *Eugenia* spp., *Artocarpus rigidus*, *Artocarpus elesticus*, *Koompassia malaccensis*, and *Xylopia* spp. have been characterized. The woods were treated with sodium meta-periodate to convert them into wood polymer composites (WPC). After two weeks the WPC were chemically treated with phenylhydrazine to convert them into secondary wood polymer composites, also called post-treated WPC (PTWPC). The chemical treatment and post-treatment are successful in improving the mechanical properties of the final product. The storage modulus (E') was measured using dynamic mechanical thermal analysis (DMTA), and the dynamic Young's modulus (E_d) was calculated using free-free vibrational testing. The results reveal that the elastic properties i.e. stiffness (E_d) and storage modulus (E') of the composite were dependent on the type of wood species. The E' of WPC and PTWPC were much higher than raw wood, whereas the glass transition temperatures (T_g) of WPC and PTWPC were much lower than those of raw wood. Free-free vibration testing provided rapid information about the quality of the composite material, such as the stiffness (E_d) of the PTWPC compared to the respective WPC and raw woods. The WPC and PTWPC were characterized using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). FTIR analysis indicated the absorption band of raw wood at 1635 cm^{-1} due to carbonyl stretching, whereas WPC and PTWPC showed increased absorption bands near 1718 cm^{-1} and 1604 cm^{-1}, respectively.

Keywords: Tropical Wood; Wood polymer composites; Post-treatment; Storage modulus; Elastic Properties; Stiffness

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INTRODUCTION

New materials in the field of wood polymer composites with their new ranges of applications represent an important basis in order to fulfill the need for creating sustainable materials from less-useful wood. Because of their low density, good mechanical performance, unlimited availability, and problem-free disposal, softwoods offer a real alternative to the well known hardwoods. Softwood specific mechanical properties are inferior compared with hardwood. The impregnation of wood with polymers results in composite materials with enhanced strength properties, dimensional stability, and resistance to bio-deterioration (Siau et al. 1965; Langwig et al. 1968; Calleton et al. 1970). Chemical coupling agents usually act as a bridge to link wood cell walls together and improve the interfacial bonding strength in WPC (Woodhams et al. 1984; Dalvag et al. 1985). Chemical agents (such as phenyl hydrazine and sodium meta-periodate) can create new structures in the WPC that influence morphology, crystallization, mechanical, thermal, biological, and other properties of WPC and PTWPC (Quillin et al. 1993; Collier et al. 1995).

Studies of the dynamic properties of wood-polymer composites have shown that the storage moduli are much higher than can be accounted for from the quantity of impregnated polymer present. Siau (1968) and Moore (1981) attributed the high modulus to the interaction between wood cell wall components and polymer. Durability of wood is directly related to its mechanical and thermal properties, which at the macro level are related to the viscoelastic properties of the wood components (polymers) (Holmberg et al. 1999).

Dynamic mechanical analysis (DMA) is a powerful technique to investigate thermal and mechanical properties of polymers. DMA permits determination of the viscoelastic behavior of wood polymers and provides valuable insights into the relationship among structure, morphology, and properties of wood polymers and their composites (Manchado and Arroyo 2000). It is understood that the viscoelastic behavior of wood depends on factors such as response of the amorphous polymers to changes in moisture content and temperature (Salmen 1984) and the response of the cellular structure to mechanical force. Dynamic mechanical analysis measures the modulus and damping properties of materials as the materials are deformed under periodic stress. The vibration technique is among the non-destructive testing (NDT) methods that are considered important in the timber industry (Halabe et al. 1995). This technique is an alternative for measuring the elastic properties and energy dissipation of wood. The method involves three types of vibration, namely bending (flexural), longitudinal (axial), and torsion, which are determined by the nature of vibration (Hearmon 1975; Bodig and Jayne 1982). Among the three types of vibration methods, the flexural vibration method is the most popular, since it is easiest to excite and detect the vibrations under investigation.

The dynamic mechanical characteristics of wood polymer composites (WPC) and post-treated wood polymer composites (PTWPC) are related to the properties of the components, the morphology of the system, and the nature of the interface between the layered cell walls and amorphous polymers such as lignin and hemicelluloses. Thus dynamic measurements can effectively be used to investigate these compatibilities and their impact on WPC and PTWPC properties. The glass transition temperature, T_g, can be defined as the temperature where: (1) the loss tangent (tan δ) is maximum; (2) the loss modulus (E'') is maximum, and (3) the inflexion points correspond to a significant drop in the storage modulus (E') (Nielsen 1974). The primary goal of the current study was to investigate the strength and stiffness of WPC and PTWPC. Softwoods are used to a great extent for the interior and domestic application. For these applications the strength and stiffness have to satisfy the requirement of low temperatures of about -100°C up to temperatures of about 60°C. For establishing such temperature-dependent material data, the DMTA is excellently suitable. In this study, Sodium meta-periodate (SMP) and phenylhydrazine were used to prepare WPC and PTWPC. The dynamic storage modulus *E'* and tan *δ* were compared with those of the raw wood. These studies also investigated the interaction between the impregnated polymer and the wood cell wall components.

EXPERIMENTAL

Materials

Five wood species were chosen for this study, among them, *Artocarpus elasticus*, *Artocarpus rigidus*, *Koompassia malaccensis*, and *Eugenia* spp. are softwoods, while *Xylopia* spp. is hardwood. These tree species were chosen because of their fast growing nature and the fact that they are easily grown in the tropics. Chemicals used to treat the wood were H_2SO_4, $NaIO_4$, and phenylhydrazine (Merck, Germany). H_2SO_4 was used as a catalyst to increase the reaction rate by its addition during specimen preparation.

Specimen Preparations

Five trees were felled, and each tree was cut into three bolts of 1.2 m long. In this work only one tree was used for each species, and the within-species variation was not studied. Only the heartwood was used. Each bolt was quarter-sawn to produce planks of 4 cm thickness and subsequently conditioned to air-dryness in a room with relative humidity of 60% and ambient temperature of around 25°C for one month prior to testing. The planks were ripped and machined to 340 mm (L) x 20 mm (T) x10 mm (R) for free-free vibration test and 10mm (L) x 2mm (R) x 7.5mm (T) specimens for dynamic mechanical thermal analysis. Only 10 replicates were used. Raw wood specimens were treated with the oxidizing agent sodium meta-periodate using an autoclave for 2 hours in order to convert them into wood-polymer composites. The oxidizing agent sodium meta-periodate penetrated into the samples and reacted with the cellulose. The temperature and pressure used were 120°C and 85 kPa, respectively. No post curing was done. The penetration of *Artocarpus elasticus*, *Artocarpus rigidus*, *Koompassia malaccensis*, *Eugenia* spp., and *Xylopia* spp. were 32%, 21.15%, 26%, 26.75, and 23%, respectively. Manufactured WPC was impregnated with phenyl hydrazine using a vacuum chamber at 25°C and 60cm Hg for 4 hours. These conditions are suitable for commercially sized samples.

Dynamic Young's Modulus Measurement

Dynamical mechanical thermal analysis (DMTA) was applied to study the effect of temperature on the storage modulus (log *E'*) and loss tangent (tan *δ*) of the woods, WPC, and PTWPC. With DMTA, which is a mechanical test, molecules in woods interact with mechanical stress. Normally all molecular relaxation processes are detected using this technique. A Perkin Elmer dynamic mechanical thermal analyzer (PE-DMTA) was used at 10 Hz frequency, x4 strains, and 2°C min^{-1} temperature rise. The rectangular specimens with moisture content around 15% were tested using a dual-cantilever bending mode on a standard bending head. The chamber surrounding the specimen at 65%RH was cooled by liquid nitrogen, and the system provided a simple thermal scan at 2°C min^{-1}

with various temperatures ranging from -100 to 200°C. The T_g was determined from the graph of tan δ versus T.

Determination of E_d was carried out using the free-free flexural vibration testing system as shown in Fig. 1. The specimen was held with AA thread according to the first mode of vibration. The specimen with an iron plate bonded at one end was set facing the driver of the electromagnet, and a microphone was placed at the centre below the specimen. The frequency was varied in order to achieve a resonant or natural frequency. The E_d was calculated from the resonant frequency by using the following equation,

$$E' = \frac{4\pi^2 f^2 l^4 A\rho}{I\,(m_n)^4} \tag{1}$$

where I = bd^3 / 12, d is beam depth, b is beam width, l is beam length, f is natural frequency of the specimen, ρ is density, A is cross sectional area, and n=1 is the first mode of vibration, where m_1=4.730.

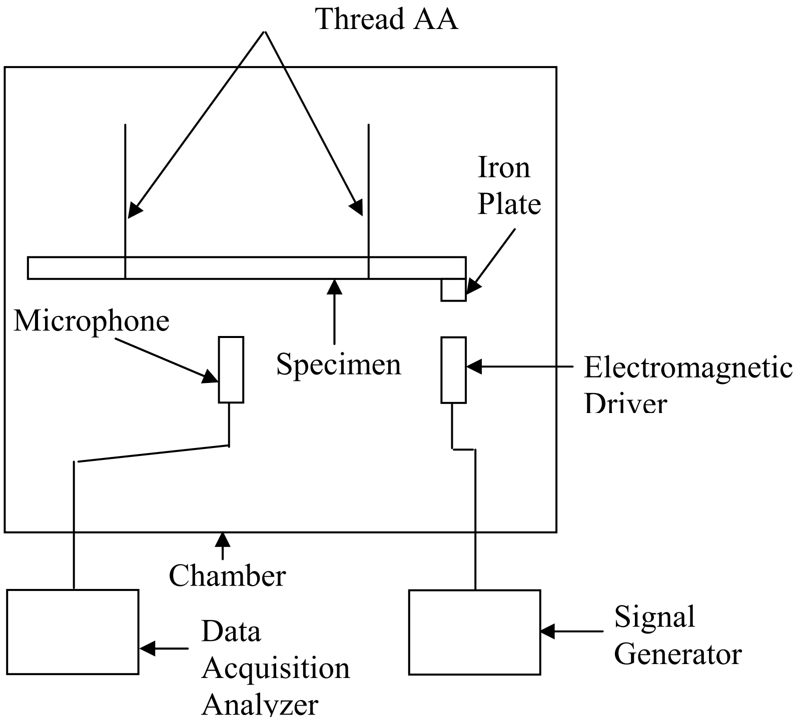


Figure 1. Free-free flexural vibration testing system

Microstructural Analysis

The infrared spectra of the raw and treated wood specimens were recorded on a Shimadzu Fourier Transform Infrared Spectroscopy (FTIR) 81001 Spectrophotometer. The transmittance range of scan was 370 to 4000 cm^{-1}. The interfacial bonding between the cellulose and sodium meta-periodate were examined using a Scanning Electron Microscope (JSM-6701F) supplied by the JEOL Company Limited, Japan. The specimens were first fixed with Karnovsky's fixative and then taken through a graded alcohol dehydration series. Once dehydrated, the specimen was coated with a thin layer of gold before being viewed on the SEM.

RESULTS AND DISCUSSION

Dynamic Young's Modulus Measurement

The viscoelastic behavior of the wood and their composites was studied by DMTA. Figure 2a-e shows the viscoelastic properties of the resulting raw wood, WPC, and PTWPC. The scales in the figures are not similar, and huge variation occurred due to the nature of the wood. Nevertheless the pattern displayed by the raw, WPC, and PTWPC softwood showed a very similar trend. One can see that for softwood the *E'* of the WPC and PTWPC was improved considerably over that of the raw wood. For all softwoods a temperature dependence was significant, involving a steep drop above 50°C. The post-treatment samples (PTWPC) showed 2 transitions, i.e. at -50°C and 100°C, because sodium meta-periodate yields a transition at 100°C whereas the post-treatment with phenyl hydrazine yields a second transition at -50°C, which occurs earlier compared to WPC, i.e. only at 100°C due to sodium meta-periodate only. This explains why the increase in *E'* values throughout the whole temperature range for PTWPC was much less as compared with WPC.

For *Xylopia* spp. (hardwood) the improvement was, however, more obvious for the PTWPC than the WPC (Fig. 2e). This indicates that interfacial bonding strength of WPC and PTWPC increased with increase of storage modulus *E'* at high retention level of polymer grafting compared with the findings of other researchers (Lu et al. 2002). The cellulose in Xylopia spp. (i.e. hardwood) is not easily oxidized with sodium meta-periodate, yielding poor inter-phase interaction with the hydrophobic polymer matrix. Upon post-treatment with phenylhydrazine the hydrophilic hydroxyl groups filled all the voids with hydrophobic polymer matrix and yielded higher *E'* value compared with WPC and raw wood. Surprisingly, upon post-treatment with phenyl hydrazine the *E'* increased three times from that of the raw wood. These higher *E'* values for PTWPC, compared to those reported by others (Yap et al. 1991), reflect crosslinking or chain scission (increase in crystallinity) caused by the impregnated phenylhydrazine. In general the *E'* values increased with the treatment and post-treatment but eventually decreased to the same value as raw wood at 200°C.

Figure 3a-e shows that raw wood had higher tan δ values than WPC and PTWPC (as seen in Fig. 3a and 3e). Loss tangent is related to the loss of energy, i.e. to viscous behavior (irreversible deformation). The lower tan δ value in WPC and PTWPC implies higher elastic recovery, which can probably be attributed to higher polymer content caused by the crosslinking resulting from the treatment. The α-transitions (100-150°C) were more prominent in the tan δ versus temperature scans. PTWPC samples were highly different from the WPC and raw wood because of their less hydrophilic nature. This observation indicates that the impregnated polymers were effectively acting as plasticizers, mainly due to their non-polar nature and relatively high molecular weight.

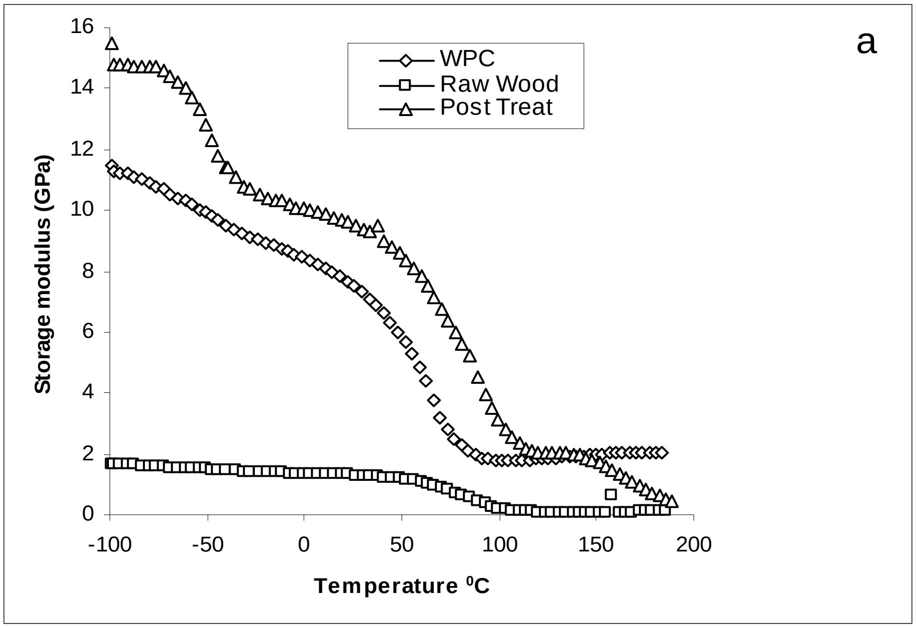


Figure 2a. *E'* versus temperature for *Artocarpus elesticus* raw wood, WPC, and PTWPC

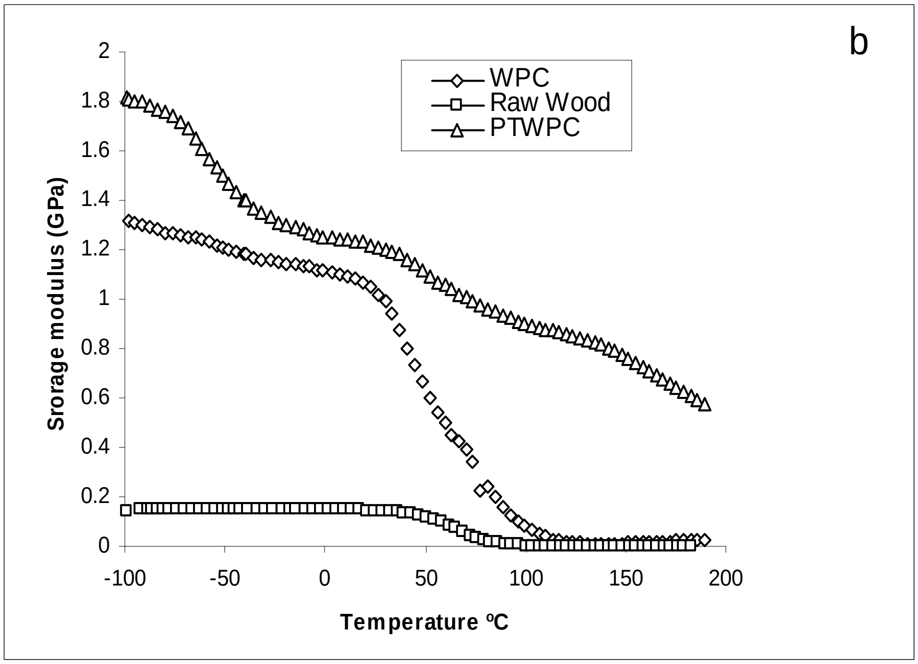


Figure 2b. *E'* versus temperature for *Artocarpus rigidus* raw wood, WPC, and PTWPC

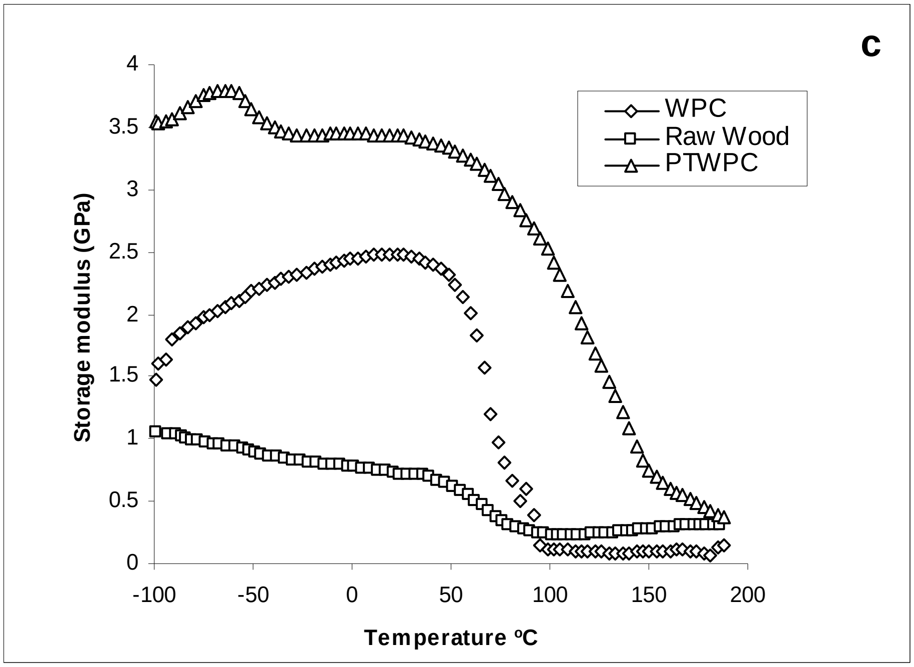


Figure 2c. *E'* versus temperature for *Koompasia malacennis* raw wood, WPC, and PTWPC

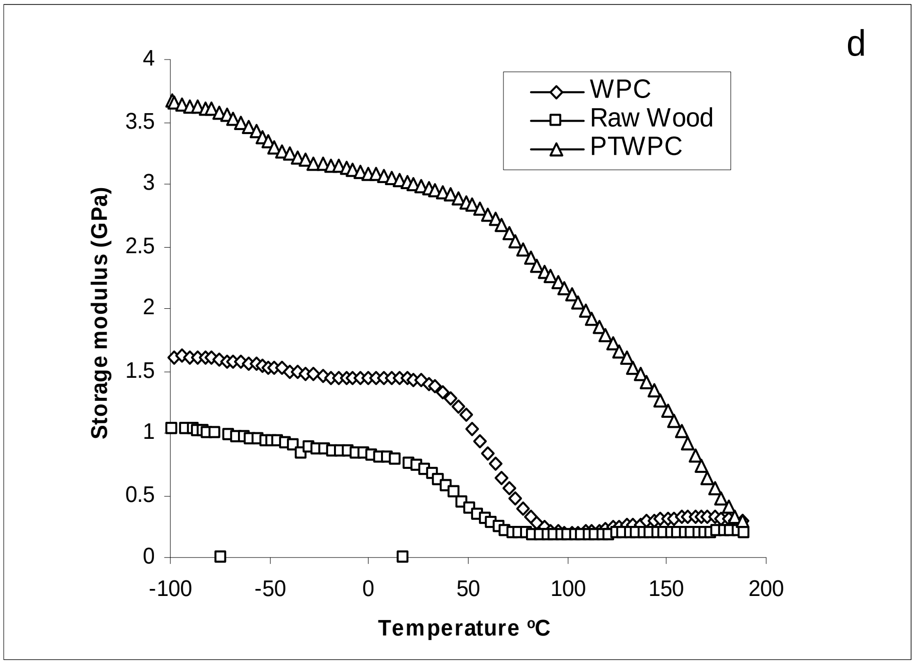


Figure 2d. *E'* versus temperature for *Eugennia* spp. raw wood, WPC, and PTWPC

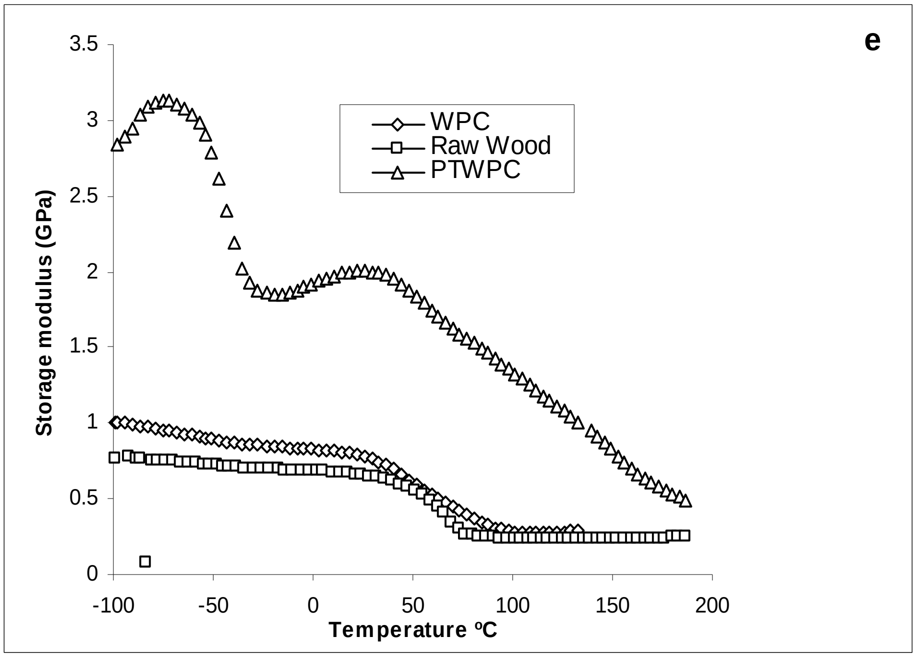


Figure 2e. *E'* versus temperature for *Xylopia* spp. raw wood, WPC, and PTWPC

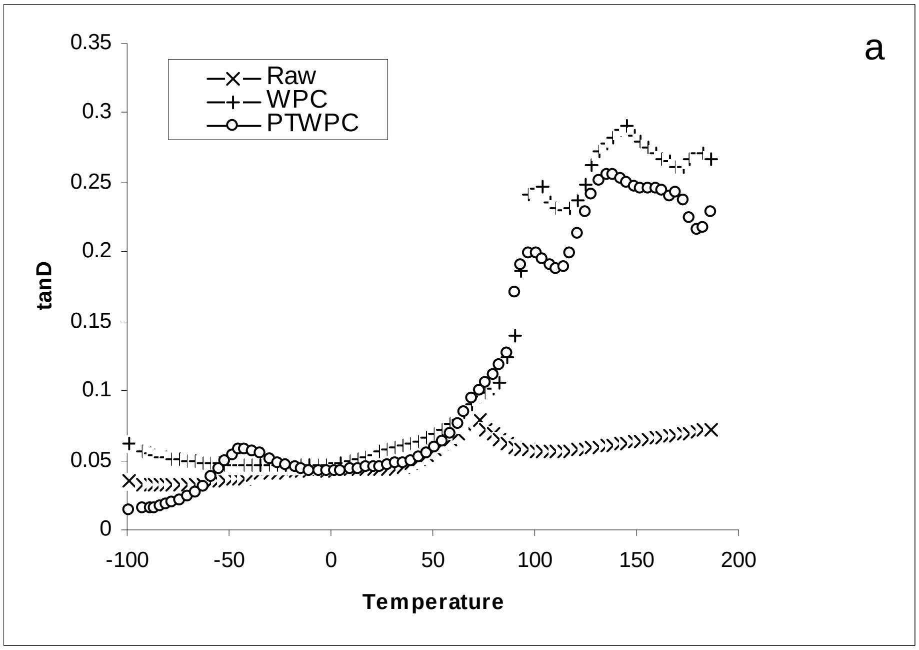


Figure 3a. Tan δ versus temperature for *Artocarpus elesticus* raw wood, WPC, and PTWPC

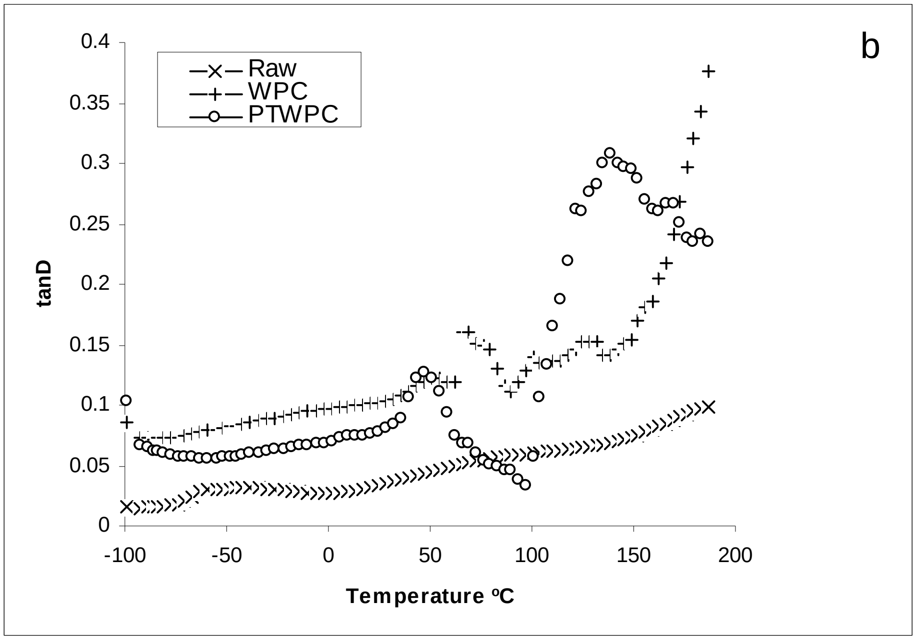


Figure 3b. Tan *δ* versus temperature for *Artocarpus rigidus* raw wood, WPC, and PTWPC

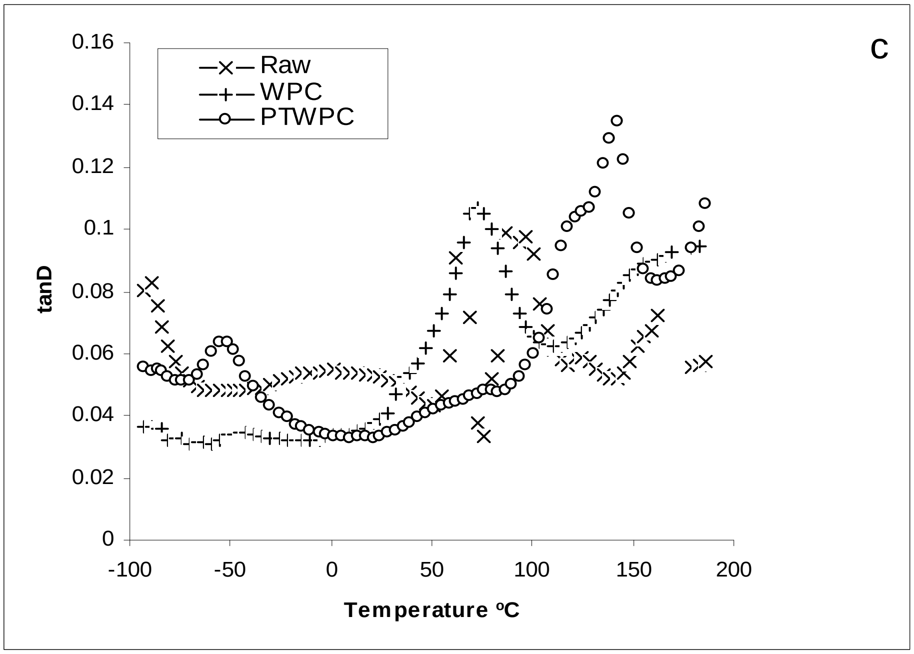


Figure 3c. Tan *δ* versus temperature for *Koompasia malacennis* raw wood, WPC, and PTWPC

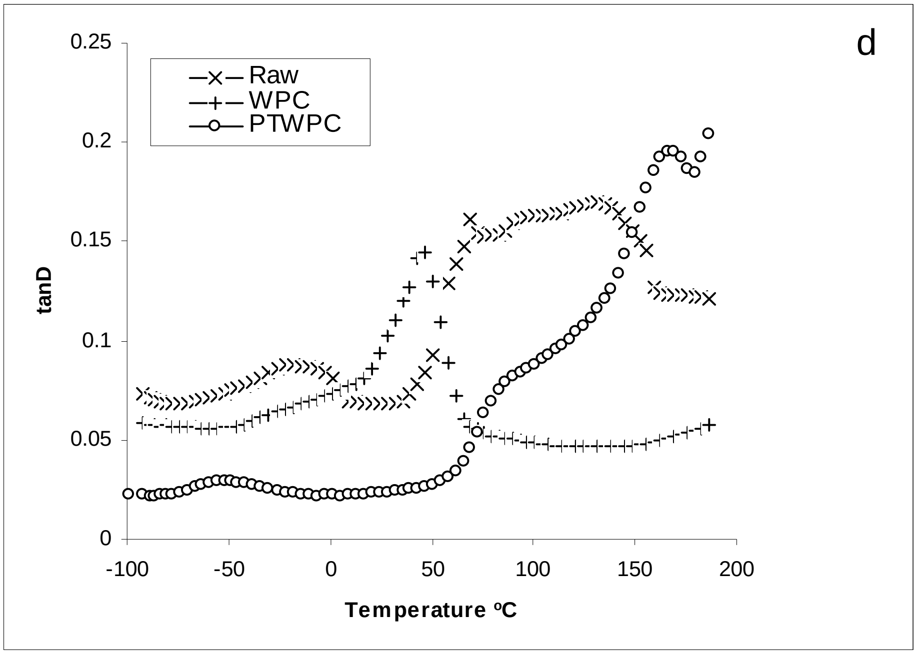


Figure 3d. Tan *δ* versus temperature for *Eugennia* spp. raw wood, WPC, and PTWPC

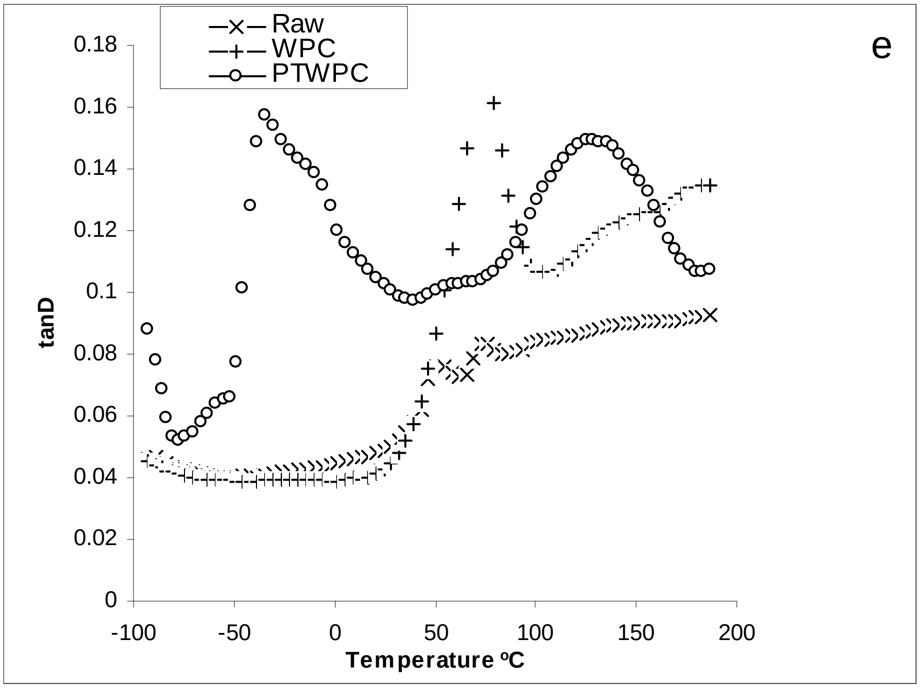


Figure 3e. Tan *δ* versus temperature for *Xylopia* spp. raw wood, WPC, and PTWPC

Assuming that the *Tg* is the temperature where tan *δ* is maximized, the raw wood showed a transition near to -50°C. The transitions at 60-70°C and 80-110°C are attributed to a secondary transition, because this is not obvious in Fig. 3a-3e (E' versus temperature). This transition has been attributed to vibration and orientation motion within the crystal (Bikiaris et al. 1999). The WPC had similar relaxation temperatures, but the relaxation occurred over broader ranges. Again this can be attributed to crosslinking and branching caused by the treatment. The addition of post-treatment to PTWPC caused a great shift in the relaxation to a higher temperature, indicating that the post-treatment increased the polymer chain mobility, thus increasing the secondary relaxation. This is interpreted as relaxation of the constrained molecules with reduced mobility close to crystallites (Bikiaris et al. 1999). In general, the post-treatment caused a shift of the tan *δ* to a higher temperature, indicating that there was an increase in the relaxation temperature. During the dynamic analysis, if the cell walls buckle, they exert a certain restorative force when amorphous polymers such as lignin and hemicelluloses are in a rubbery state.

The stiffness of the raw wood, WPC, and PTWPC from the free-free flexural vibration testing system is shown in Fig. 4(a-e). The treatments by sodium meta-periodate only slightly increased the Young's modulus, as seen in all species. The storage modulus was significantly affected by the treatment (see Fig. 2a-2e), but the elastic properties showed significant changes only in *Artocarpus elesticus*. Further treatment with phenylhydrazine enhanced the Young's modulus for all species.

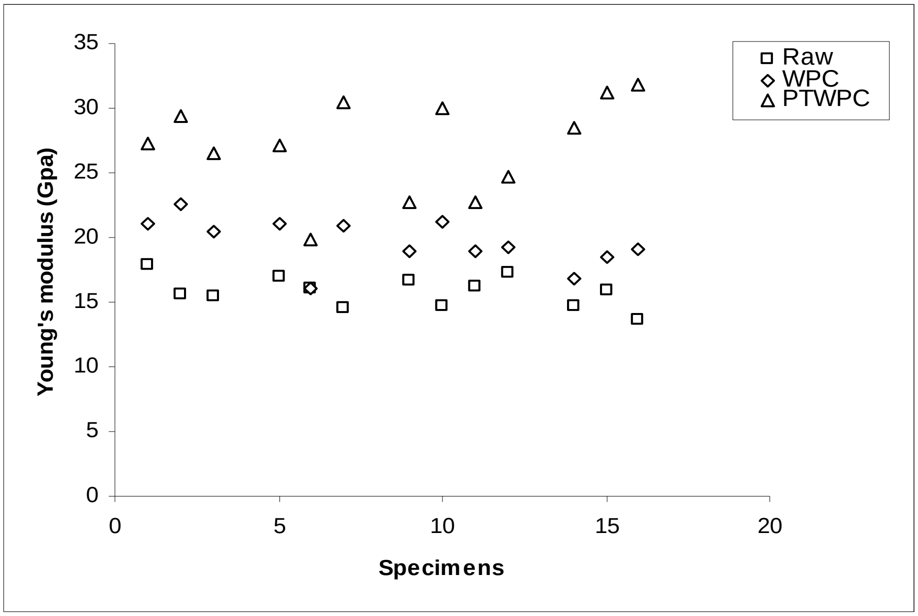


Figure 4a. E_d of *Artocarpus elesticus* raw wood, WPC, and PTWPC

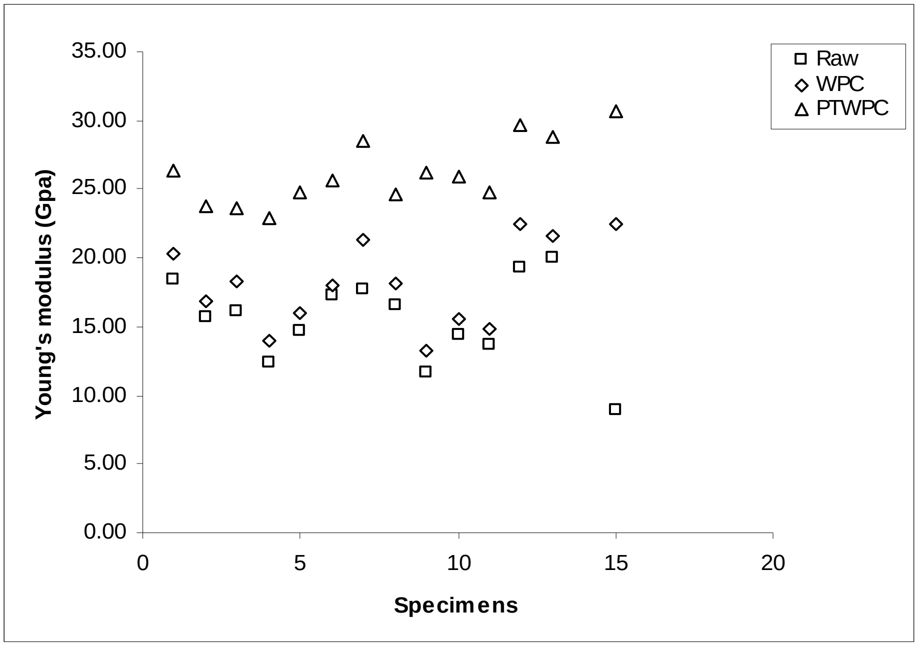


Figure 4b. E_d of *Artocarpus rigidus* raw wood, WPC, and PTWPC

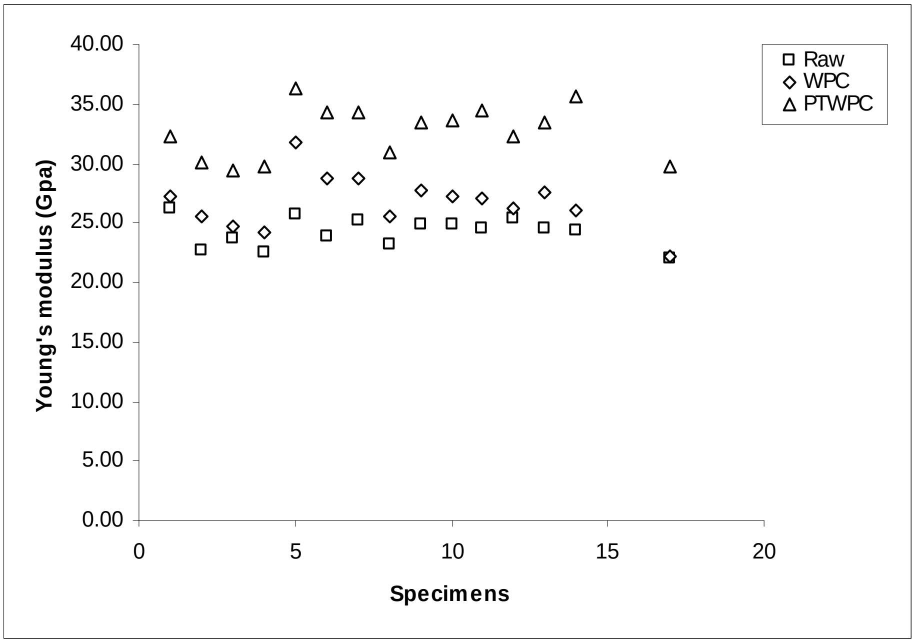


Figure 4c. E_d of *Koompasia malacennis* raw wood, WPC, and PTWPC

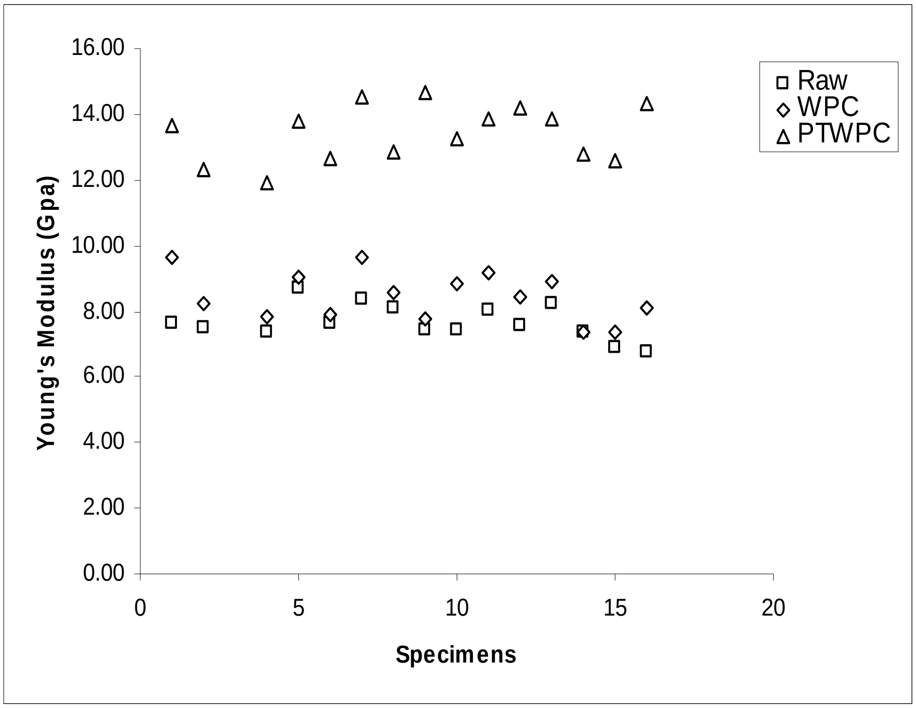


Figure 4d. E_d of *Eugennia* spp. raw wood, WPC, and PTWPC

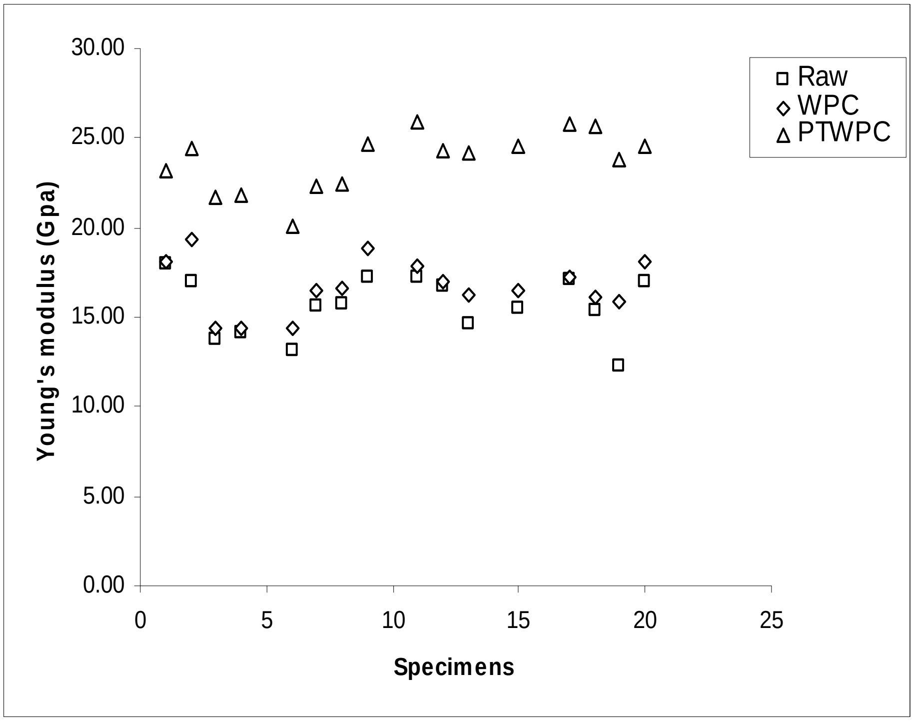


Figure 4e. E_d of *Xylopia* spp. raw wood, WPC, and PTWPC

Microstructural Analysis

Figure 5a-c shows the FTIR spectrum for the raw, WPC, and PTWPC for *Artocarpus elesticus*. The characterizations were performed on all species, but similar results were obtained. Thus only the results corresponding to *Artocarpus elesticus* are shown as a representative case. The reactions of sodium meta-periodate with cellulose in raw wood fiber at 120°C and 85 KPa pressure yielded the oxidized product, 2, 3-dialdehyde cellulose. Sodium meta-periodate not only impregnated the wood specimens but also reacted with hydroxyl groups of the cellulose and produced 2,3-dialdehyde cellulose. Dialdehyde cellulose filled up the void spaces within the wood structure and produced WPC. This was confirmed by the FTIR spectroscopic analysis of the raw and treated wood fiber (Fig. 5a-b). The IR spectrum of the WPC clearly shows the characteristic band of an aldehyde group in the regions of 2906 cm^{-1} and 2850 cm^{-1} due to C-H stretching and in the region of 1734 cm^{-1} due to carbonyl stretching. The IR spectrum of the raw wood fiber (Fig. 5a) shows the absorption band near 1735 cm^{-1}. This absorption band is due to the carbonyl group of acetyl ester in hemicellulose and carbonyl aldehyde in lignin (Ismail et al. 2002). However, there was also an increased absorption band near 1718 cm^{-1}. This increased absorption band may be due to the carbonyl aldehyde of dialdehyde cellulose, which is formed by the oxidation of wood fiber as shown in Fig. 5b.

The formation of dialdehyde can be explained as due to three hydroxyl groups in the cellulose anhydroglucose unit. One is the primary hydroxyl group at C_6 and other two are the secondary hydroxyl groups at C_2 and C_3. The primary hydroxyl group is more reactive than the secondary ones, so the cleavage of the anhydroglucose ring between carbons 2 and carbon 3 results in the formation of dialdehyde. The IR spectrum of the PTWPC (Fig. 5c) shows that the absorption band of 3431 cm^{-1} is the symmetric stretch of an NH_2 group in 2,3 diphenylhydrazo cellulose due to the carbonyl stretch at 1604 cm^{-1}. This clearly indicates that oxidize specimens were successfully impregnated with phenylhydrazine.

Figure 6 shows the chemical reaction between cellulose and sodium metaperiodate, producing dialdehyde cellulose. Upon post-treatment with phenylhydrazine the dialdehyde cellulose becomes 2,3-diphenylhydrazo cellulose. Figure 7a-b shows the SEM micrographs for the typical softwood and hardwood. The micrograph of raw softwood (*Artocarpus rigidus*) shows drastic changes after treatment, as shown by the WPC. This is in accordance with the drastic increase of *E'* values (WPC) after treatment (Fig. 2b). After post-treatment (PTWPC) the changes of the microstructure were less significant, as also being shown by the less drastic increase of *E'* in PTWPC. On the other hand, the SEM micrograph of raw hardwood (*Xylopia* spp.) was less affected after the treatment. Surprisingly, the post-treatment changed the microstructure drastically, and obviously these changes strengthened the PTWPC, as seen in the *E'* values (Fig. 2e). These findings confirm the small increment of *E'* values in WPC.

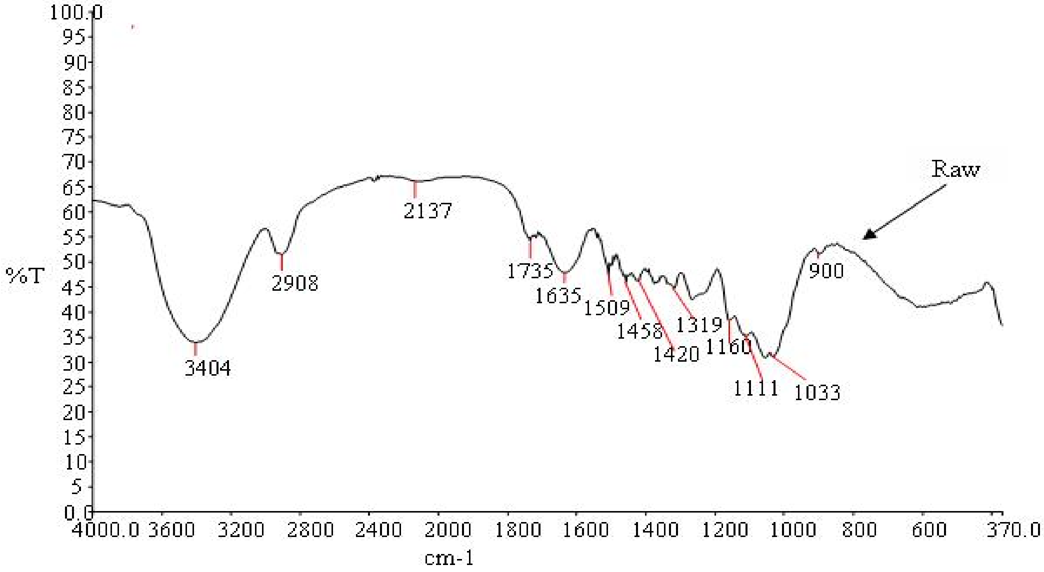


Figure 5a. FTIR spectrum for the raw wood

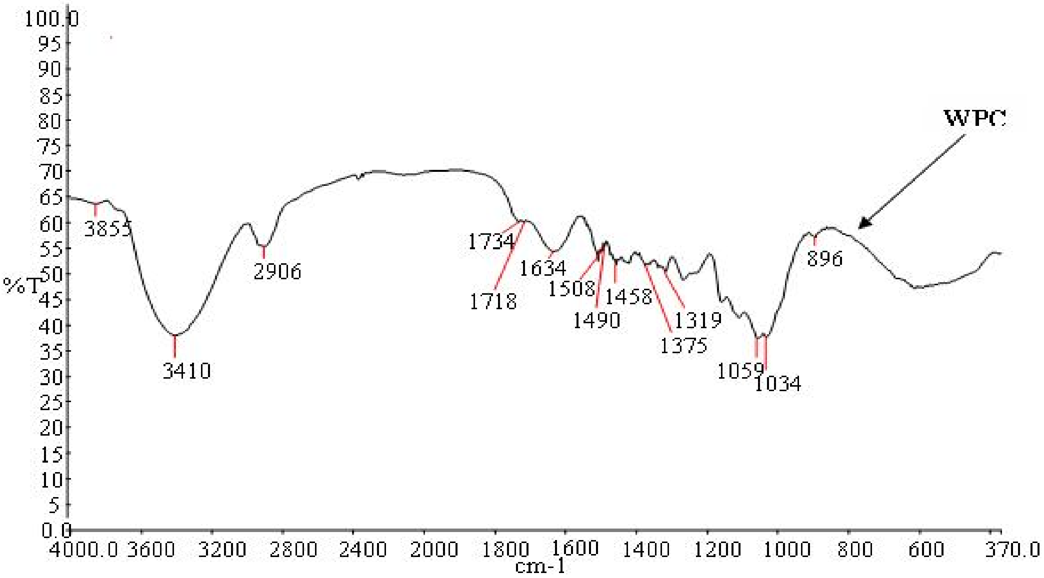


Figure 5b. FTIR spectrum for WPC

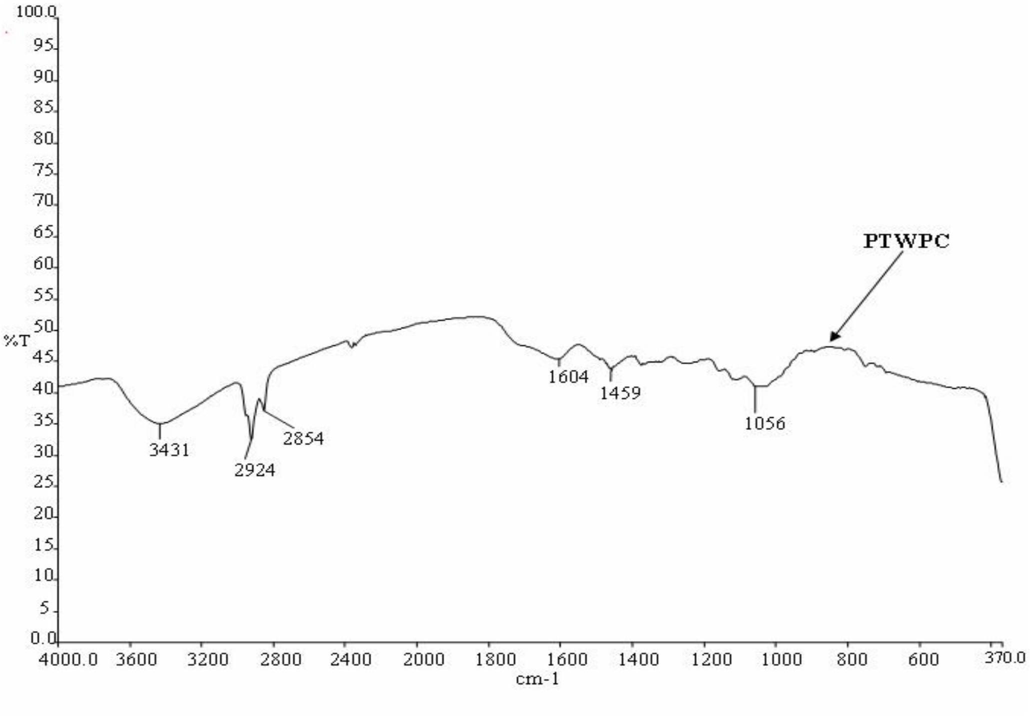


Figure 5c. FTIR spectrum for PTWPC

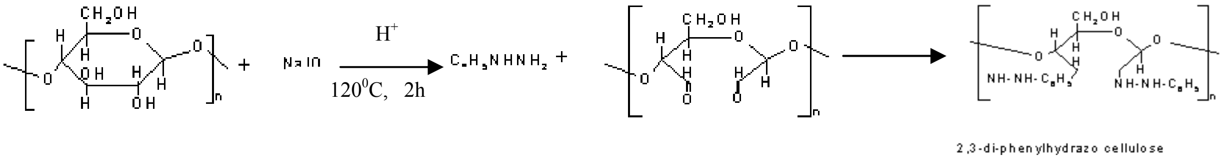
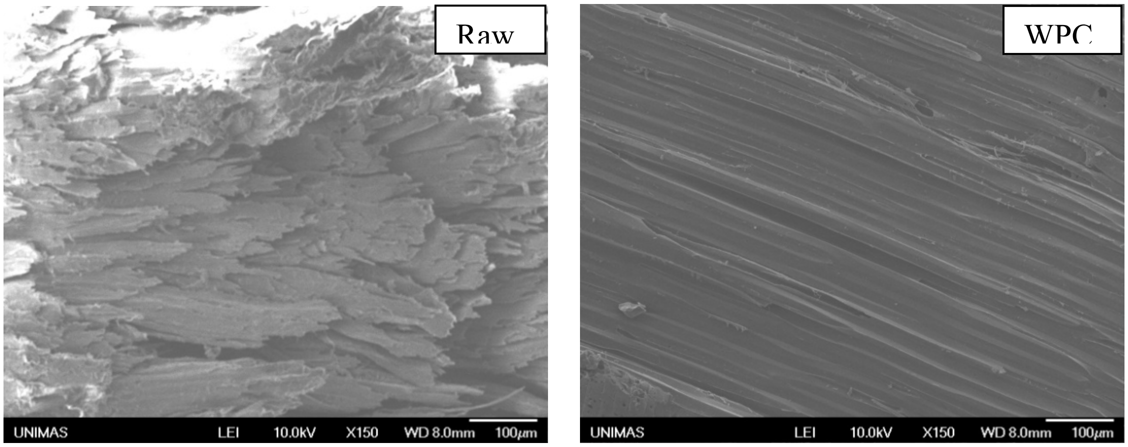


Figure 6. Oxidation of raw wood fiber specimens with sodium metaperiodate and phenylhydrazine



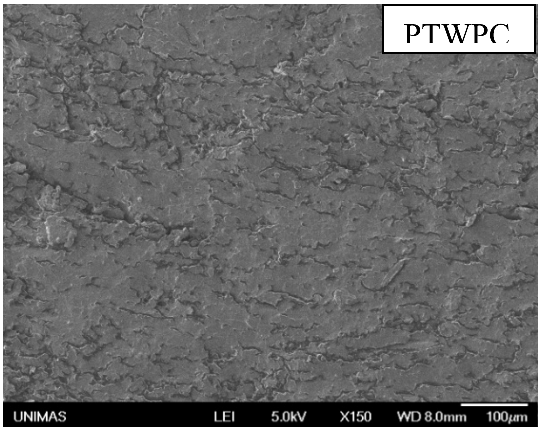


Figure 7a. SEM micrograph for typical softwood (*Artocarpus rigidus*)

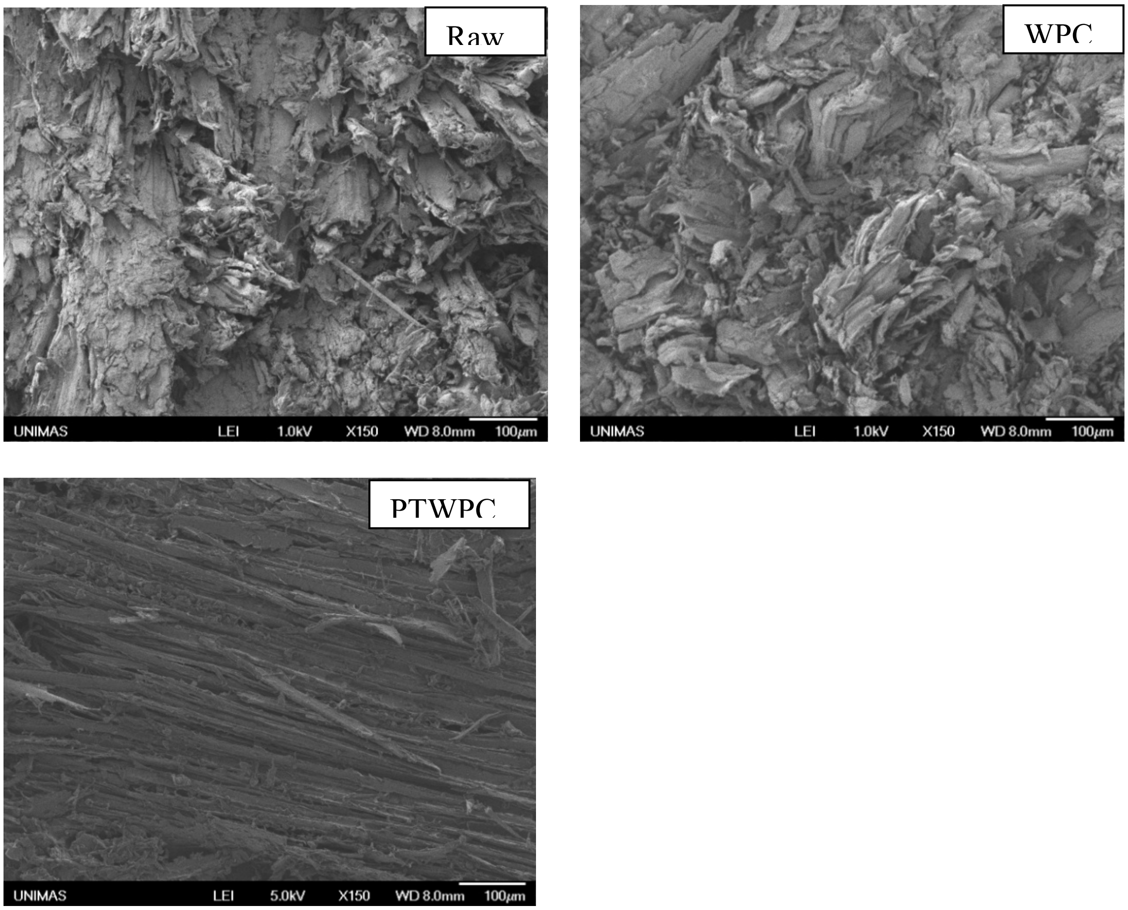


Figure 7b. SEM micrograph for typical hardwood (*Xylopia* spp.)

CONCLUSION

It can be concluded that the *E'* and E_d values for all the selected tropical wood species studied were strongly increased by the post-treatment. This means that *E'* and E_d values, depending on degree of polymerization, can be further improved with further post-treatments. *E'* values of all WPCs except *Xylopia* spp. (hardwood) were consistently larger than for raw wood, which means that sodium meta-periodate successfully converted raw wood to WPC in softwood. Upon further post-treaments with phenylhydrazine the *E'* values of all PTWPCs including *Xylopia* spp. (hardwood) were consistently larger than WPC, which means that with phenylhydrazine it was possible to successfully convert WPC to PTWPC. In general the sodium meta-periodate slightly improved the E_d values of raw wood, but surprisongly the phenylhydrazine significantly raised the value of the E_d for PTWPC. However, in the present study, the trend of the E_d was similar to *E'* for hardwood (*Xylopia* spp.), which showed that hardwood viscoleastic properties and stiffness were less affected by the sodium meta-periodate. All selected tropical wood species exhibited glass-like properties (high modulus) at low temperatures and rubbery properties (low modulus) at higher temperatures. The glass transition temperature of raw wood species ranged from 50 to 70^{o}C. Upon treatment with sodium metaperiodate the glass transition temperature increased and became significantly higher when treated with and phenylhydrazine.

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