

Assessment of the Physico-mechanical, Thermal, and Morphological Properties of Rubber Wood Modified with Silica Sol in Combination with GU/GMU Resins

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Rubber wood was modified with both a combination of silica sol and glyoxal urea (S-GU), and a combination of silica sol and glyoxal melamine urea (S-GMU). The physico-mechanical properties were measured. Thermal properties, chemical molecular structure, and cellular morphology were analyzed *via* thermogravimetry (TG), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The weight percent gain (WPG) increased as the concentration of the impregnated aqueous solutions increased. The S-GMU treated wood exhibited a greater WPG than the S-GU treated wood at the same concentration. Anti-swelling efficiency (ASE), modulus of elasticity (MOE), and modulus of rupture (MOR) of treated wood increased as the WPG increased. The highest ASE value was 42.0%, for the S-20%GMU treated wood, which was higher than the S-20%GU treated wood. The MOR of the S-20%GMU treated wood was improved by 25%. Thermal analyses showed the thermostability of S-GMU treated wood increased. FTIR results indicated the presence of C-N and Si-O-Si bonds in the S-GMU treated wood, and the lignin and carbohydrates degraded to a certain extent. SEM imaging showed that the S-GMU was deposited in the cell lumen and cell wall. Therefore, this study produced evidence of an improvement in the physico-mechanical and thermal properties of S-GMU treated wood.

Keywords: Rubber wood; Modification; Silica sol; Glyoxal-urea resin; Glyoxal-melamine-urea resin

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INTRODUCTION

Rubber trees (*Hevea brasiliensis*), which are indigenous to the Amazon valley of South America, have been widely cultivated in China since the latter half of the 20th century (Qin *et al.* 2017). Currently, they are primarily planted in Hainan, Yunnan, and other southern Chinese provinces, covering more than 1.18 million ha (Jiang *et al.* 2018). Generally, rubber trees are replanted every 25 years to 30 years, when they become uneconomical for harvesting for latex production. The felled trees have been used as lumber for furniture and building materials in recent years (Salla *et al.* 2012; Min 2019). However, the rubber wood has inferior dimensional stability compared to other woods and is prone to decay, warp deformation, and cracks. Modifying the rubber wood is a good method for improving its properties and achieving a greater range of potential use.

Various chemical modifications have been proposed, including esterifications (Berube *et al.* 2018), etherifications (Hill 2007), silylation (Donath *et al.* 2006), and impregnation with thermosetting resin (Wang *et al.* 2017). Some of those have been used in a commercial application, such as wood modification *via* a thermosetting resin. Numerous studies have used low-molecular-weight phenol-formaldehyde resin (PF),

melamine-formaldehyde resin (MF), urea-formaldehyde resin (UF), or melamine-urea-formaldehyde resins (MUF) to improve the physico-mechanical and thermal properties of various woods (Deka and Saikia 2000; Yue *et al.* 2016). However, because formaldehyde-based thermosetting resins pose major environmental concerns, it is necessary to replace the toxic formaldehyde in the synthesis of environmentally friendly wood adhesives. Among the various aldehydes available, the usage of glyoxal has yielded the best results, as it is nontoxic, has a low cost, is nonvolatile, and is easily biodegradable (Younesi-Kordkheili and Pizzi 2016; Younesi-Kordkheili and Pizzi 2017). Due to its two active merged aldehyde groups, it can be used to glyoxylate the lignins in cell walls or cross-link with the hydroxyl groups in cellulosic materials *via* a hemiacetal or acetal reaction in the presence of a catalyst (Lee and Kim 2005; Navarrete *et al.* 2013). Some researchers have used glyoxal as a cross-linking agent for wood modification, and all modified woods exhibited excellent dimensional stability and poor moisture absorption. The acidity of glyoxal at high curing temperatures may cause hydrolysis or degradation of the cell wall (Nakano 1993; Dong *et al.* 2014). Glyoxal-based synthetic resins are also much more environmentally friendly than formaldehyde-based thermosetting resins. Glyoxal readily combines with urea to form synthesized GU resin, which improves the mechanical properties of wood samples. However, the anti-leachability of GU-treated woods decreases (Yan *et al.* 2015).

Silicon is an abundant element that can form a wide variety of inorganic compounds. Modification with inorganic silicon compounds can enhance the dimensional stability of the wood and improve its antimicrobial properties and fire resistance (Saka *et al.* 1992; Mai and Militz 2004; Donath *et al.* 2006). Silica itself is hydrophilic. To increase the hydrophobicity of the inorganic silica particle, the surface is modified by different silane compounds (Hu *et al.* 2004). Nano-SiO₂, was used in studies, as well, to improve the mechanical, water uptake, dimensional stability, hardness, and flammability properties of wood-polymer composites (WPCs) (Devi *et al.* 2012; Dong *et al.* 2014). In addition, impregnating wood with silica sol. The nano-sized sols are easily transportable into wood and from coatings on the inner wood surfaces (Liu *et al.* 2015). The silica particles improve the surface hydrophobicity *via* the presence of film-forming substances (Kumar *et al.* 2017). Wood modification with silica sol can also enhance the flexure properties and surface hardness of the wood, as well as improving its dimensional stability, decay resistance, and water-related properties (Temiz *et al.* 2006; Tejado *et al.* 2007; Qu *et al.* 2011; Kumar *et al.* 2016).

Organic-inorganic treatment is an emerging method of wood modification *via* physical-chemical methods to achieve improved dimensional stability, mechanical properties, and the addition of new functions. For this purpose, an environment-friendly GMU resin was synthesized from glyoxal, melamine, and urea, and the resulting resin was applied to rubber wood in combination with silica sol for the first time. The aim of this study was to investigate the physico-mechanical, thermal, and morphological properties of the modified rubber wood and to better understand the modification mechanism *via* Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) analysis.

EXPERIMENTAL

Materials

The rubber wood (*Hevea brasiliensis*) was collected from Ledong County, Hainan Province, China. Rubber wood blocks with dimensions of 300 mm × 20 mm × 20 mm (longitudinal × radial × tangential) were prepared from clear, defect-free wood. To reduce deviation, all samples were chosen from the same timber and machined (sawn and planed) at the same time.

The silica sol was obtained from the Guangzhou Suize Environment Protection Technology Co., Ltd. (Guangdong, China) with an average particle size of 14 nm to 30 nm and a pH range of 9.5 to 10.5. The glyoxal-urea (GU) resin and glyoxal-melamine-urea (GMU) resin with a solid content of 40% (a pH: 7.5 to 8.5, a viscosity of 2.5 mPa·s to 5.0 mPa·s, a water miscibility greater than 10, and a shelf life of 30 d) were both synthesized in a laboratory. All of the chemicals and solvents used in this study were of analytical grade.

Preparation of the Modified Wood

Preparation of impregnation solutions

The impregnated aqueous solutions were obtained by mixing silica sol and GU resin or GMU resin under an ultrasonic wave. The aqueous solutions were ratioed as follows: (1) 10% silica sol; (2) 10% silica sol and 5%, 10%, or 20% GU resin; and (3) 10% silica sol and 5%, 10%, or 20% GMU resin.

Samples treatment

All of the samples were initially dried at 103 °C ± 2 °C to ensure a constant weight. Afterwards the dimensions and weights were measured.

Impregnation

The samples were placed into a stainless reactor and subjected to vacuum for 30 min. The respective impregnation aqueous solution was introduced to the stainless reactor, and the sample was submerged under a pressure of 0.95 MPa for 5 h at room temperature. After impregnation, the pressure of the stainless reactor was relieved, and the aqueous solution was removed.

Polymerization

The wood samples were wrapped with aluminum foil, kept at room temperature for 4 to 5 d, and placed into an oven at 100 °C for 24 h for polymerization. Afterwards, the aluminum foil was removed and the sample was dried at, 103 °C ± 2 °C until constant weight was obtained. The dimensions and weights were then measured.

Physico-Mechanical Properties

Weight percentage gain (WPG) was used as an essential parameter for the characterization of wood samples. The WPG was calculated based on Eq. 1,

$$WPG = \frac{W_1 - W_0}{W_0} \times 100\% \quad (1)$$

where W_0 is the oven-dried weights of samples before modification and W_1 is the oven-dried weights of samples after modification. Each type of sample was measured by 15 tests.

Dimensional stability was evaluated by measurement of anti-swelling efficiency (ASE). Each type of sample was measured with 15 tests. ASE was evaluated according to Chinese standard GB/T 1934.2 (2009). The ASE was calculated as follows, according to Eq. 2,

$$ASE = \frac{S_0 - S_1}{S_0} \times 100\% \quad (2)$$

where S_0 is the volume expansion of the untreated samples and S_1 is the volume expansion of the treated samples. During the tests, the dimensions of each specimen was 20 mm x 20 mm x 20 mm (L x T x R).

Mechanical testing was conducted using an INSTRON 5582 universal testing machine (Instron Co., Grove City, PA, USA). The modulus of elasticity (MOE) and the modulus of rupture (MOR) were determined *via* a three-point bending test with specimens measuring 300 mm x 20 mm x 20 mm (L x T x R) according to Chinese standards GB/T 1936.2 (2009) and GB/T 1936.1 (2009). Fifteen replicates were tested for each treatment.

Thermal Analysis

The treated and untreated wood samples were ground into powder and sieved with a 40 mesh to 60 mesh size. Thermogravimetry and differential scanning calorimetry were performed under a N_2 atmosphere at a heating rate of 10 °C/min (from room temperature to 800 °C) using an SDT Q600 (simultaneous DSC-TGA) thermal analyzer (TA Instruments, Waters LLC, New Castle, DE, USA).

Microstructural Characterization

Scanning electron microscopy (Hitachi, S-4800, Toyko, Japan) was performed to characterize the distribution in the cross sections, radial sections, and tangential sections of the silica sol-treated wood and the S-20% GMU-treated wood. The elemental distribution and contents of the untreated and treated wood were analyzed via a SEM (Quanta, FEG 650, Hillsboro, OR, USA) linked to an energy-dispersive X-ray analyzing system with an Oxford Instruments X-maxN 150 EDX detector with an acceleration voltage of 5 kV. The scanning surface of the samples had dimensions of 2 mm x 2 mm x 5 mm and were smoothed with a sliding microtome.

RESULTS AND DISCUSSION

Physico-Mechanical Properties

As shown in Table 1, the WPG of the modified wood increased as the concentration of the silica sol-GU/ GMU aqueous solutions increased. The WPG of the modified wood samples impregnated with silica sol combined with GU ranged from 18.4% to 24.2%, which were higher than the WPG of the modified wood samples impregnated with only silica sol. A similar trend was obtained by Yan *et al.* (2015) for poplar wood with GU combined with nano-SiO₂. However, the wood treated with S-GMU exhibited a greater WPG than the S-GU treated wood at the same concentration, and the highest WPG was 28.3% (S-20 % GMU). Furthermore, the ASE of the modified wood increased as the WPG increased. The highest ASE was 42.02% for the S-20 % GMU treated wood samples, which was higher than the other wood samples subjected to silica sol and S-GU treatments. For the mechanical properties, the MOE and MOR of the modified wood samples increased as

the WPG increased, as shown in Table 1. The MOE and MOR of the untreated wood samples were on average 9320 MPa and 91.8 MPa, respectively. The MOE and MOR of the wood samples impregnated with a S-20% GMU solution were 9640 MPa and 115.0 MPa, respectively. The MOR of the S-20% GMU treated wood samples was improved by 25% when compared to the untreated wood samples. This indicated that the S-GMU treatment could improve the physico-mechanical properties.

Table 1. The Physico-Mechanical Properties of the Untreated and Treated Wood

| Sample | Treatment Concentration | WPG (%) | ASE (%) | MOE (MPa) | MOR (MPa) |
|---------|--------------------------|--------------|--------------|------------------|---------------|
| C | untreated | - | - | 9323.88 ± 348.15 | 91.79 ± 4.30 |
| S | 10% silica sol | 16.29 ± 0.85 | 29.49 ± 1.35 | 9401.38 ± 388.68 | 95.31 ± 3.78 |
| S-5GU | 10% silica sol + 5% GU | 18.39 ± 1.05 | 32.12 ± 1.49 | 9442.15 ± 360.48 | 96.82 ± 3.72 |
| S-10GU | 10% silica sol + 10% GU | 22.56 ± 1.53 | 34.12 ± 1.62 | 9511.28 ± 405.63 | 99.84 ± 4.00 |
| S-20GU | 10% silica sol + 20% GU | 24.21 ± 1.88 | 36.73 ± 1.82 | 9527.91 ± 364.56 | 102.67 ± 5.16 |
| S-5GMU | 10% silica sol + 5% GMU | 20.08 ± 0.88 | 33.16 ± 1.21 | 9489.28 ± 347.20 | 98.32 ± 3.24 |
| S-10GMU | 10% silica sol + 10% GMU | 25.41 ± 1.37 | 38.69 ± 1.37 | 9542.65 ± 371.26 | 105.69 ± 3.65 |
| S-20GMU | 10% silica sol + 20% GMU | 28.32 ± 1.93 | 42.02 ± 1.81 | 9636.20 ± 375.18 | 114.96 ± 3.81 |

Each value represents the average of 15 samples ± standard deviation
 Untreated:treated with water

Thermal Stability

Thermal analysis was performed to examine the thermal stability of the untreated and treated wood. A better thermal stability means that the wood undergoes pyrolysis at a higher temperature and/or at a slower rate at a particular temperature. As shown in Fig. 1, it could be seen that the TG and differential thermogravimetry (DTG) curves of the thermal degradation process were divided into three mass loss stages. In the first stage, from 30 °C to approximately 120 °C, the mass loss resulted from the removal of water (Wang *et al.* 2017). The mass losses were 2.94%, 2.10%, 1.52%, and 1.71% for the untreated, silica sol, S-20% GU, and S-20% GMU wood samples, respectively. The S-20% GMU wood samples had a lower value than the untreated wood samples. In the second stage, the temperature range was from 120 °C to 380 °C, which corresponded primarily to the decomposition of the hemicellulose and cellulose into char residues and CO₂, CO, CH₄, CH₃OH, as well as CH₃COOH, *etc.* (Qu *et al.* 2011). In this stage, the mass loss of the untreated wood was 83.1%, which was higher than the mass loss of the treated wood samples. That indicated that the thermal stability of the treated wood had slightly increased. In addition, the temperature that corresponded to the maximum rate of the mass loss of the treated wood (349.2 °C for the S-20% GMU samples) was less than the mass loss of the untreated wood samples (363.1 °C), and the maximum rate of mass loss decreased. The third stage occurred in the temperature range of 380 °C to 800 °C, which was due to the degradation of lignins. The residue char at 800 °C was 6.15%, 26.85%, 28.70%, and 32.27% for the untreated,

silica sol, S-20% GU, and S-20% GMU wood samples, respectively. The increase in residue was more obvious in the S-20 % GMU wood samples.

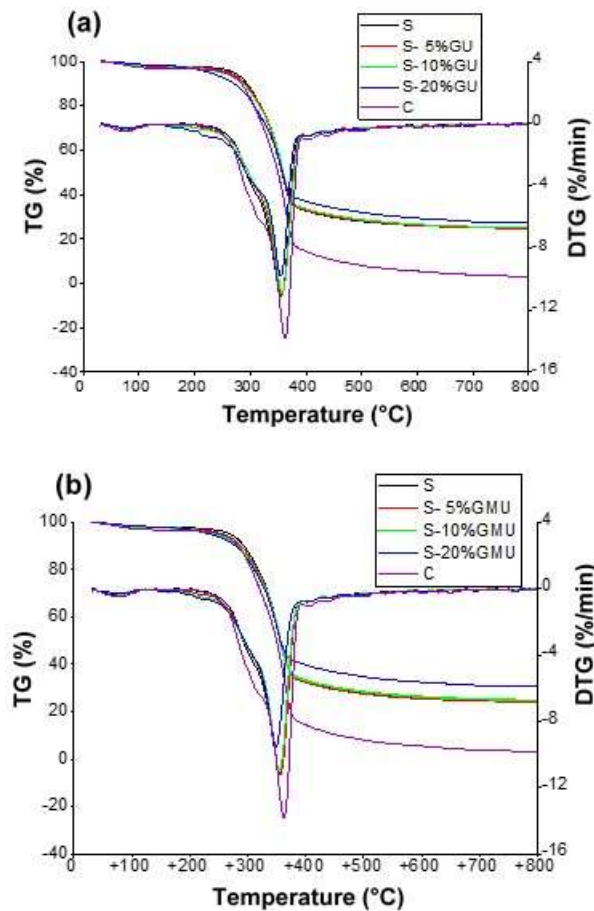


Fig. 1. The TG and DTG curves of the untreated wood samples, silica sol-treated wood samples, and wood samples treated with S-GU (a) and S-GMU (b)

The DSC results for the untreated wood, silica sol-treated wood, S-GU treated wood, and S-GMU treated wood are shown in Fig. 2. As shown, the DSC curve of the untreated and treated wood exhibited a similar curve trend. The endothermic peak at approximately 100 °C was primarily attributed to the removal of moisture. When compared with the untreated samples and the S-GU and S-GMU treated wood samples, the peak of the silica sol-treated wood was the largest, which indicated a stronger endothermic reaction in the nitrogen atmosphere. In addition, there was an obvious peak range from 300 °C to 400 °C in the DSC curve, which primarily corresponded to the decomposition of hemicellulose and cellulose.

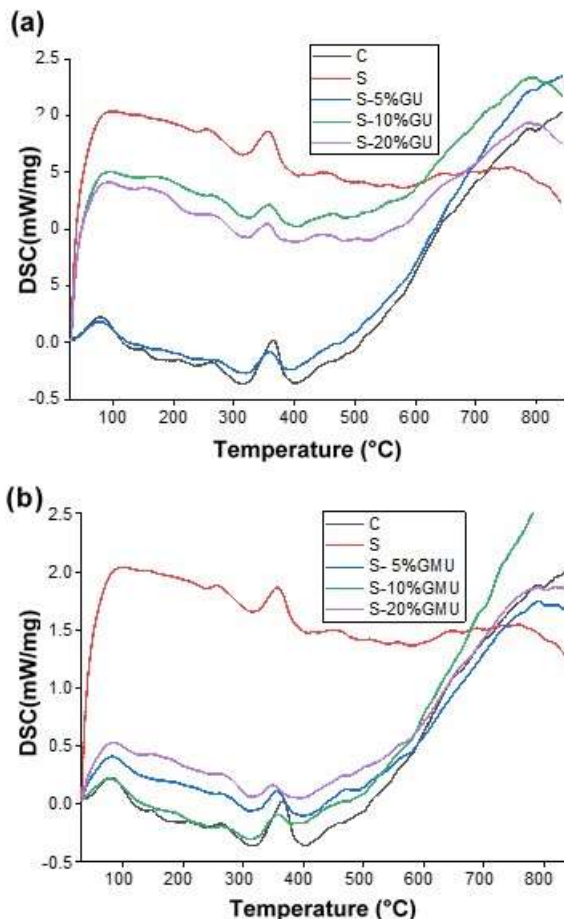


Fig. 2. The DSC of the untreated wood samples, silica sol-treated wood samples, and wood samples treated with S-GU (a) and S-GMU (b)

Table 2 showed the initial pyrolysis temperature (T_i), peak temperature (T_m), and peak area (S_q) of the untreated and treated wood samples. There was a minor difference between the T_i and T_m of the treated and untreated wood samples. However, the S_q values of the S-20% GMU treated wood samples were lower when compared to the untreated wood samples. In addition, the S_q values were $84.7 \text{ J} \cdot \text{g}^{-1}$ and $23.1 \text{ J} \cdot \text{g}^{-1}$ for the untreated and S-20% GMU treated wood samples, respectively.

Table 2. Differential Scanning Calorimetry Analysis

| Samples | C | S | S- | | | | | |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | | 5GU | 10GU | 20GU | 5GMU | 10GMU | 20GMU |
| Ti/°C | 327.3 | 320.4 | 325.9 | 327.2 | 327.3 | 320.9 | 326.3 | 322.3 |
| Tm/°C | 365.4 | 356.2 | 359.9 | 358.8 | 355.7 | 355.9 | 356.9 | 348.2 |
| Sq/J-g-1 | 84.7 | 82.7 | 41.9 | 31.5 | 22.9 | 73.6 | 40.3 | 25.1 |

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier transform infrared spectroscopy was used to characterize the chemical changes of the wood before and after modification. The assignments of the characterized IR absorption peaks in the wood are shown in Table 3 (Cai *et al.* 2007; Tejado *et al.* 2007; Deng *et al.* 2014a,b; Yan *et al.* 2015; Jiang *et al.* 2018; Sun *et al.* 2019).

Table 3. FTIR Assignments of the Untreated and Treated Wood

| Absorption Band (cm ⁻¹) | Chemical Structure Assignments |
|-------------------------------------|---|
| 3200 to 3600 | N-H, O-H stretching vibration |
| 2900 | C-H stretching vibration |
| 1740 | C=O stretching vibration |
| 1656 | C=O stretching vibration |
| 1510 | Benzene ring stretching vibration in lignin |
| 1463 | C-N stretching vibration |
| 1244 | C-N and N-H stretching vibration |
| 1055 | C-N stretching vibration |
| 470 | Si-O and Si-O-Si stretching vibration |

As shown in Fig. 3, the C-H stretching vibration band at 2900 cm⁻¹ from the methyl and methylene groups in the modified wood samples decreased when compared with the band in the untreated wood samples. In comparison with the untreated and silica sol-treated wood, the intensity of the band near 1740 cm⁻¹, which was assigned to C=O, increased in the S-GMU treated wood samples, which indicated that more C=O bonds formed in the modified wood (Yan *et al.* 2015). In addition, due to the p- π conjugation effect between the -NH₂ and C=O in the GU and GMU resins, the C=O peak shifted to a lower wavenumber of 1740 cm⁻¹ (Deng *et al.* 2014a). Furthermore, the bands at 1656 cm⁻¹ and 1510 cm⁻¹ decreased in intensity. The peaks of the S-GU treated wood samples had a more obvious decreased than the S-GMU treated wood samples did. That indicated that the lignins and carbohydrates degraded to a certain extent in the modified wood samples and the S-GMU-treated wood exhibited the least total degradation.

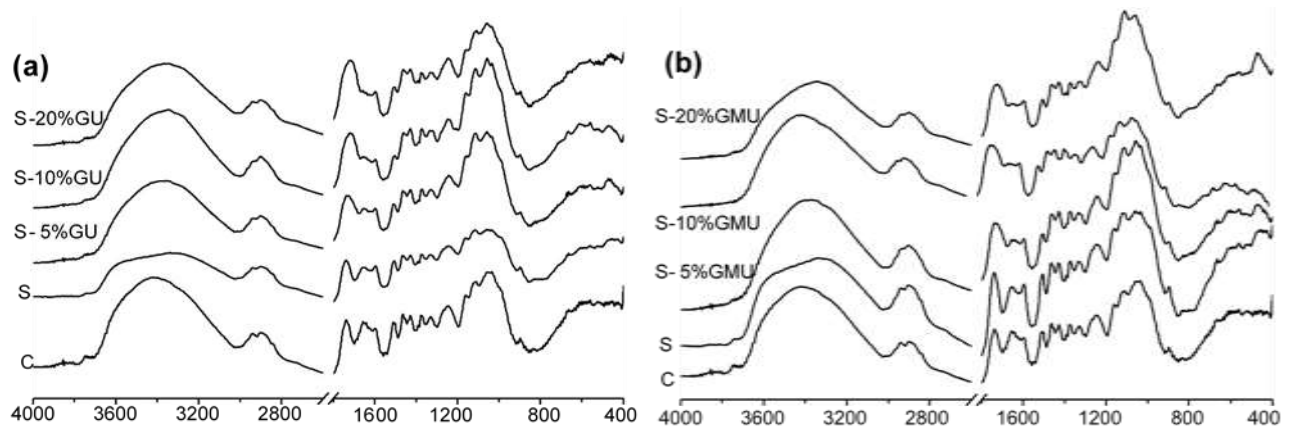


Fig. 3. The FTIR spectra of the untreated wood samples, silica sol-treated wood samples, and wood samples treated with S-GU (a) and S-GMU (b)

Microscopic Analysis

Figures 4 and 5 show the morphologies of the untreated wood, and the wood with silica sol or S-20% GMU at different magnifications. Empty cell walls, pits, and distinct lacunae were obvious in the untreated wood (Fig. 5a), while these empty places in the treated wood were occupied by the resin or nano-SiO₂ materials.

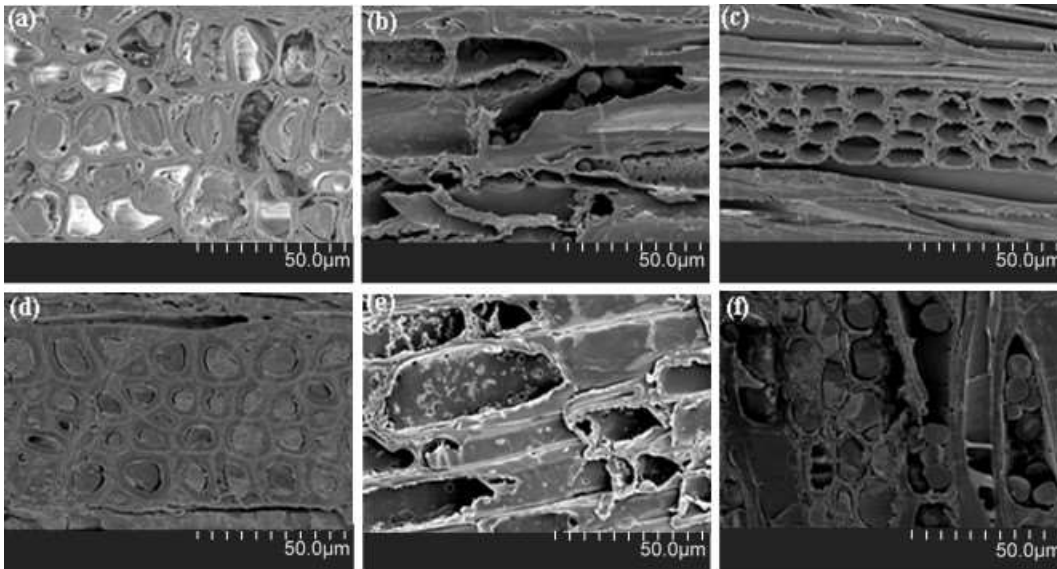


Fig. 4. The SEM micrograph of the silica sol-treated wood samples: (a) cross section, (b) radial section, and (c) tangential section. The SEM micrograph of the S-20% GMU-treated wood samples: (d) cross section, (e) radial section, and (f) tangential section

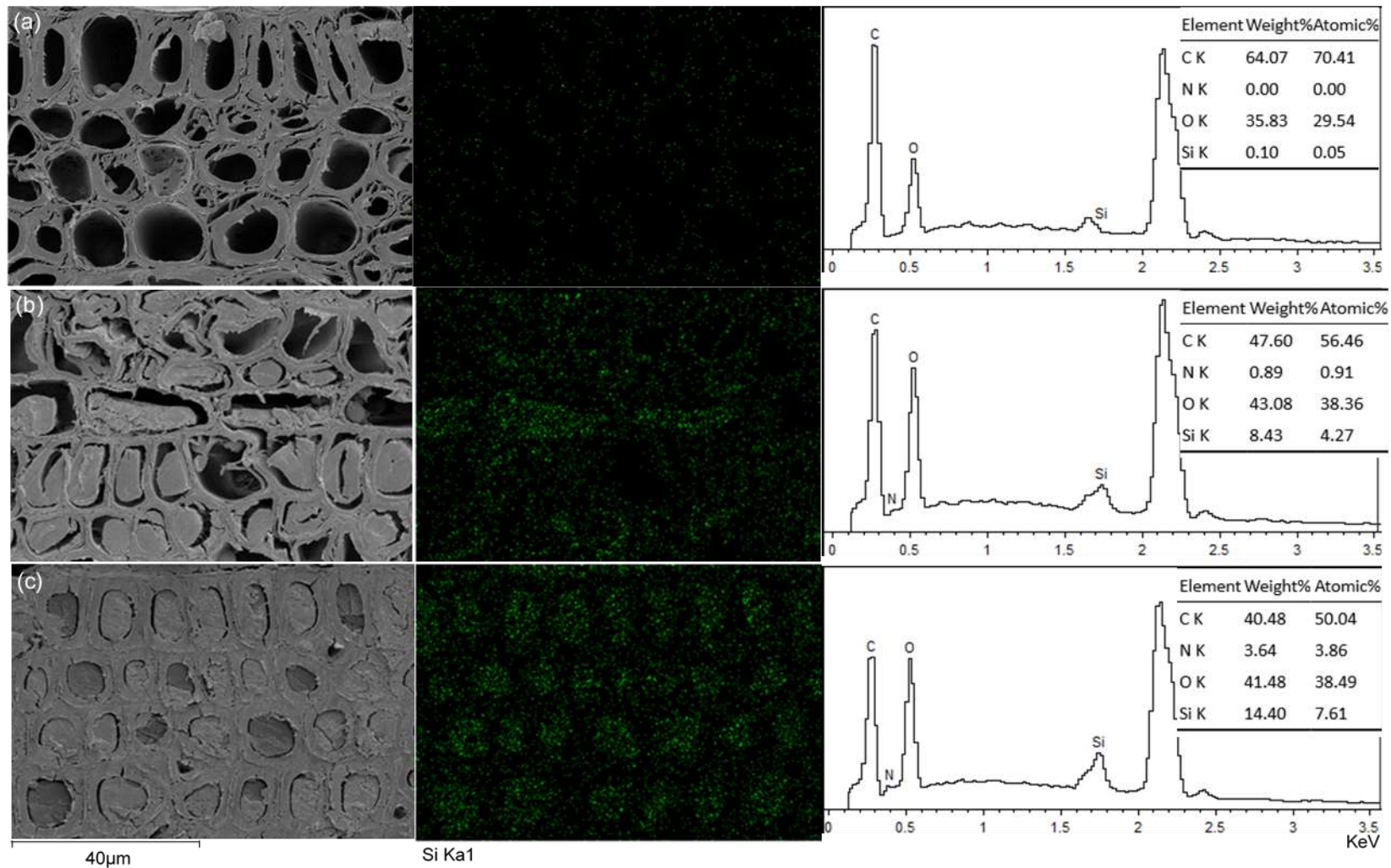


Fig. 5. The SEM-EDX analyses of the distribution of silicon and other elements in the untreated wood (a), silica sol-treated wood (b), and S-20% GMU-treated wood samples (c)

The SEM images of the cross sections, radial sections, and tangential sections of the silica sol-treated wood samples and the S-20 % GMU-treated wood samples are shown in Fig. 4. The SEM images showed that the treatment solution was taken up and fixed into the wood matrix. Most of the treatment solution was deposited in the cell lumen, while portions of it coated the surface of the cell wall after the treatment. For the S-20% GMU treated wood samples, more of the silica sol-GMU aqueous solution filled in the cell lumen and attached to the surface of the cell wall than did in the silica sol-treated wood samples. And the polymer is well-distributed in the wood cell lumen and cell wall. This may act as barrier to prevent water molecule to penetrate the wood structure which is probably due to the deposition of some resin solid content in the lumen of cells in the wood.

The SEM-EDX analyses of the distribution of silicon and other elements in the untreated wood (a), silica sol-treated wood (b), and S-20% GMU-treated wood samples (c) are shown in Fig. 5. There was only a small amount deposited in the cell walls of the untreated wood samples, which was probably due to exposure to silicon during sample treatment (as shown in Fig. 5a). Based on SEM-EDX results, silicon content was about 0.10%; however, Si were 8.43% and 14.40% in the silica sol-treated wood and S-20% GMU treated wood, respectively. Silicon was not only successfully introduced into the wood cell lumens, but also into the cell walls, thus influencing the mechanical properties of the modified wood. There was a greater amount of Si deposited in the cell lumen and cell wall of the S-20 % GMU-treated wood samples compared to the silica sol-treated wood samples. This was due to the fact that the GMU resin had a positive effect on silicon fixation in the wood matrix. In addition, the weight of the total nitrogen in the S-20% GMU treated wood samples increased when compared to the silica sol-treated wood samples. This could be attributed to the composition of the GMU resin containing melamine and urea.

CONCLUSIONS

1. Rubber wood was modified with both a combination of silica sol and glyoxal melamine urea (S-GMU). The physical and mechanical properties of modified materials were improved. This process of rubber wood using GMU and silica sol is feasible for the preparation of an effective product with improved properties.
2. SEM-EDX analyses showed that the silica sol-GMU aqueous solution was incorporated into wood and diffused in the wood lumen and cell walls. The GMU resin had a positive effect on silicon fixation in the wood matrix. FTIR results showed that the presence of C-N and Si-O-Si bonds in the S-GMU treated wood samples was detected.
3. The TGA analysis showed that the total mass loss that occurred during thermal decomposition of the S-GMU treated wood samples was lower than the untreated wood samples, and the thermostability of the S-GMU treated wood increased more than the S-GU treated wood samples.
4. All mechanical properties of the modified wood samples improved further, facilitated by the silica sol unique three-dimensional network, and favourable properties (flame resistance and high stability). The silica sol-GMU aqueous solutions were deposited in the cell lumen and the cell wall, which could block the path available for water access

to cell walls, which could result in a deceleration of moisture sorption and improve the anti-swelling efficiency.

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