Impact of Freeze and Silicone Oil Treatments on Hygroscopic and Chemical Components of Two Fast-Growing Species

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Abstract:

The objective of this work was to study the impacts of freezing and silicone oil treatments in relation to hygroscopic and chemical constituents of two fast-growing (*Firmiana simplex* L. and *Pinus massoniana* L.) wood species. Five experiments were carried out and then compared to control: Freezing-treatment (F), freezing-silicone oil treatments (FSOT180 and FSOT210) and silicone oil treatments (SOT180 and SOT210). The freezing-treatment phase was conducted at -22 °C for 168 h and silicone oil treatment phase at 180 and 210 °C for 4 h. Hygroscopic properties and chemical constituent were determined. The hygroscopicity of the treated woods were decreased and their chemical structures were transformed. The high treatment temperature degraded the chemical constituents of the wood and XRD showed that the amorphous cellulose was affected in the treated wood. This study revealed that silicone oil and freezing treatments could be used to improve the wood properties of the selected wood species.

1. Introduction

Wood is a natural product utilized for construction due to its abundance and good strength properties. The major advantage of wood with regards to its usage as an engineering material is the high strength potentials [1]. Dimensional instability due to moisture changes, lack of durability due to attack by biodegrading agents, weathering and differential shrinkage [2] are some of the disadvantages encountered in wood

utilization [3]. To overcome the above stated disadvantages, modification of wood i.e silicone oil heat treatment combined with freeze treatment is considered a viable option for enhancing the wood properties for utilization for technological applications [4,5,6,7].

The objective of modification of wood is to alter the properties of wood to enable it to overcome certain disadvantages caused by the behaviour of the wood. The functionalization adds new properties to the wood such that at the expiration of the lifecycle of the bio-material, it should be disposed without causing any detrimental impact to the environment. Interest in wood modification is not new, as study conducted by Tiemann [8] showed that the drying of wood at certain level temperatures diminished the moisture content and the resultant swelling of wood.

With regards to thermal treatment of wood with oil, the method can enhance wood properties through the synergy of the oil and heat [9]. Wood modification with oil as heating medium has demonstrated the following advantages: oil is an efficient heating medium because of its capacity to transfer heat to wood more evenly, isolate oxygen from wood all through the treatment process [9], checks the incidence of oxidative process [10,11] and many oils have higher boiling points compared to the temperature needed for thermal modification, thus making it suitable for oil heat treatment (OHT) of wood [12]. The effectiveness of OHT is anchor on factors: thermal modification conditions, wood species, oil types and retention [9,13] while the degree of effectiveness is dependent on treatment temperature usually between 180 - 260°C compared to treatment time.

Recently, freeze-treatment has attracted some research interest and has successfully been used to decrease shrinkages [14]. Furthermore, combined techniques of wood treatment are adopted in the last few years to enhance wood technological properties [14,15]. This including pre-treatment of wood by freezing followed by thermal treatments [17]. During freeze-treatment, green wood is cool up to -90 °C in the cooling chamber of a refrigerator before drying it in an oven at 103 °C [7]. Freezing-treatment combined with silicone oil treatment can significantly modify the wood properties of fast-growing wood.

This work is aimed at comparing the hygroscopic and chemical constituents of two fast-growing (*Firmiana simplex* and *Pinus massoniana*) woods as a result of the impacts of freezing and silicone oil treatments. Results from this work will serve as a guide in the treatment of wood using two-step freeze-silicone oil treatment in the wood industry.

2. Materials and Experiments

2.1. Material Preparation

In this research, two fast-growing wood species (Chinese parasol, *Firmiana simplex* L.) and (Masson pine, *Pinus massoniana* L.) were investigated. They are one of the most important subtropical timber species predominantly abundant in South-eastern Asia and are widely used in wood industries but have low economic value due to their less durability. The wood properties can be improved through freezing treatment combined with silicone oil treatment with potential industrial applications. The dimension of the woods were 20 mm (tangential) × 20 mm (radial) × 50 mm (longitudinal) according to ISO 3129 [18]. Prior to treatments, the woods were

stabilized in conditioning chamber to 30 ± 5%. Table 1 shows the basic properties of the two-fast-growing wood species investigated in this study.

Table 1. *Basic properties of Chinese parasol and Masson pine.*

Wood materials	Chinese parasol (*F. simplex*)	Masson pine (*P. massoniana*)
Density (kg/cm^3)*[a]	286	428
Hemicellulose (wt%)	26.40	23.75
Cellulose (wt%)	41.97	43.61
Lignin (wt%)	22.56	25.10

[a] *Dry basis*

2.2. Experimental procedure

Experiments for the wood treatment were composed of two parts which included freezing-treatment and silicone oil treatment as indicated in Table 2. The freezing-treatment phase was conducted according to Missio et al. and Okon and Okon [7,19] with slide modification. In the refrigerator, freezing temperature increased from 23 °C to -22 °C with cooling rate of 0.07 °C min.[-1]. The freezing rate ranged between the temperature ∼3 °C to ∼22 °C. 280 samples were frozen for 7 days at stabilized freeze temperature of -22°C. Freeze-treated samples were removed, allow to defrost and oven-dried at 60 °C to constant moisture content.

Table 2. *Treatments parameters of control and freeze-silicone oil treated wood.*

	Freezing-treatment phase			Silicone oil treatment phase		
Treatments	Condition	Temperature (°C)	Time (h)	Condition	Temperature (°C)	Time (h)
Control	-	-	-	-	-	-
F	Wet	-22	168	-	-	-
FSOT180	Wet	-22	168	Climate chamber (20°C and 65%)	180	4
FSOT 210	Wet	-22	168	Climate chamber (20°C and 65%)	210	4
SOT 180	-	-	-	Climate chamber (20°C and 65%)	180	4
SOT 210	-	-	-	Climate chamber (20°C and 65%)	210	4

F-freezing-treatment, FSOT- freeze-silicone oil treatment, SOT- silicone oil treatment

Silicone oil treatment phase was performed in this research based on a trial experiment and earlier researches by Okon et al. [4,5] in a closed oil bath chamber. Silicone oil aided heat transfer and was pre-heated at 180 and 210 °C with samples immersed. After treatment for 4 h, the samples were removed, cooled in a desiccator and kept in a humidity chamber (20 °C and 65% RH).

Combined freeze-silicone oil treatments (FSOT) was conducted using the methods described above for freezing-treatment and silicone oil treatment. Table 2 indicate that 5 treatments were conducted, then compared with the control.

2.3. Hygroscopic Properties Analysis

Shrinkage and water absorption of the control and freeze-silicone oil treated samples were conducted using ASTM D 143-94 [20] and ASTM D 570 [21]. The control and treated samples were oven-dried and then kept in a humidity chamber at 20 °C and 65% relative humidity (RH) for moisture stability. 10 samples were used for individual treatment, with samples size of 20 mm × 20 mm × 50 mm immersed in water for 168 h at 20±1°C. Before and after immersion in water the samples were weighed and dimension taken. The volumetric shrinkage coefficient was determined using equation (1):

$$S\ (\%) = \frac{d_i - d_f}{d_i} * 100$$

(1)

Where S = shrinkage coefficient, d_i = initial green dimension before treatments (mm), d_f = oven-dried dimension after treatments (mm).

Water absorption was calculated using equation (2):

$$WA\ (\%) = \frac{W_{Sat} - W_{dry}}{W_{dry}} * 100$$

(2)

Where WA = water absorption, W_{dry} = samples weight before soaking in water, W_{Sat} = samples weight after soaking water.

2.4. Chemical Components Analysis

Chemical constituents of control and freeze-silicone oil treated samples were analyzed using Fourier transform infrared (FTIR), thermogravimetric and X-ray diffraction (XRD) analyses. The wood samples were chipped, grinded and sieved to pass through a 12– 45 mesh prior to analyses. The sieved wood samples were oven-dried at 103 °C to remove moisture. Afterwards, the samples were placed in plastic zip-lock bags and stored in air-tight container until experiments were conducted. FTIR of control and freeze-silicone oil treated samples were analyzed using Nicolet 380 spectrophotometer (Thermo Electron Instruments, USA). FTIR spectra were taken between 4500 - 500 cm^{-1}, with a spectral resolution of 4 cm^{-1} and 32 scans per run. Thermogravimetric analysis (TGA) was carried out using thermogravimetric analyzer (NETZSCH 44, Germany), 7 mg samples were loaded while the analysis started from 23°C to 600°C. The rate of Nitrogen flow was 70 mL min^{-1} while heating rate was 12 °C min^{-1}. XRD was obtained using Rigaku Ultima IV X-ray diffractometer with monochromatic Cu Kα_{1+2} radiation (λ= 0.1542 nm), from 5- 45° (2θ range) with a scanning rate of 4° min^{-1} at 60kV and electric current 50 mA. The crystallinity index (C_rI) of the samples were calculated using equation (3) [4]:

$$C_rI\ (\%) = \frac{I_{200} - I_0}{I_{200}} * 100$$

(3)

Where, I_{200} is maximum intensity of diffraction angle in the crystalline plane, I_0 is the intensity of diffraction angle in the amorphous plane.

2.5. Data Analysis

Hygroscopic properties data were analyzed using one-way Analysis of Variance (ANOVA) with Duncan post-test use to access the influence of the treatments on the hygroscopic properties at p-value of 0.05. Before subjecting the data to ANOVA percentages were arcsine-transformed.

3. Results and Discussion

The results of shrinkage for freeze-silicone oil treated and control wood samples are presented in Figure 1, to give information on the shrinkage (dimensional stability) of the samples. The tangential shrinkage, radial shrinkage and volumetric shrinkage coefficient of the freeze-silicone oil treated wood declined significantly with regards to the control. FSOT210 and SOT210 treatments had the lowest shrinkage coefficient with reference to the control. The shrinkage of *F. simplex* wood decreased by 63.07, 59.14 and 61.47% and 60.93, 58.37 and 60.17% in tangential, radial and volumetric directions for FSOT210 and SOT210 treatments respectively (Figure 1), while shrinkage of *P. massoniana* wood decreased by 78.41, 66.40 and 65.62% and 61.48, 62.64 and 61.93% in tangential, radial and volumetric directions for FSOT210 and SOT210 treatments respectively. FSOT210 and SOT210 treatments of *F. simplex* and *P. massoniana* woods presented significant reduction in water absorption (Figure 2). The same reduction were observed in FSOT180 and SOT180 treatments. The water absorption of *F. simplex* wood decreased by 34.19, 25.96 and 20.43% and 66.82, 55.40 and 50.39% in tangential, radial and volumetric shrinkages for FSOT210 and SOT210 treatments while water absorption of *P. massoniana* wood decreased by 88.51, 86.78 and 86.37% and 91.42, 90.81 and 89.35% in tangential, radial and volumetric shrinkages for FSOT210 and SOT210 treatments respectively. From these results, it is deduce that freeze-silicone oil treatments have significant effects on the shrinkage and water absorption of *F. simplex* and *P. massoniana* woods. The decrease in hygroscopicity of both wood may be attributed to the water repellency of silicone oil [4]. Decrease in the hygroscopicity of the wood maybe due to oil uptake and deposition of oil in the cell wall thus forming a protective layer on the wood [9]. Treatments with heating step presented reduced hygroscopicity compared to treatments with freezing step, this implies that high temperatures played significant role in the modification of *F. simplex* and *P. massoniana* woods. Previous studies have reported decrease hygroscopicity at high temperatures, this is because less water is absorbed by the cell wall due to the degradation of hydroxyl groups [22,23]. It was noted that freezing step did not completely modify the chemical constituent of the wood, with regards to degradation of hydrophilic groups [6]. However, decrease in hygroscopicity may be due to crosslinking caused by polycondensation reactions in lignin and limited availability of hydroxyl groups to water molecules which lead to high crystallinity [24,25,26,27,28]. Furthermore, the major effect of freezing step is a reversible physical enlargement of vessels and permeability of frozen wood [29], nevertheless combined freeze-silicone oil treatments can result in a fast elimination of water molecules inside the structure of wood.
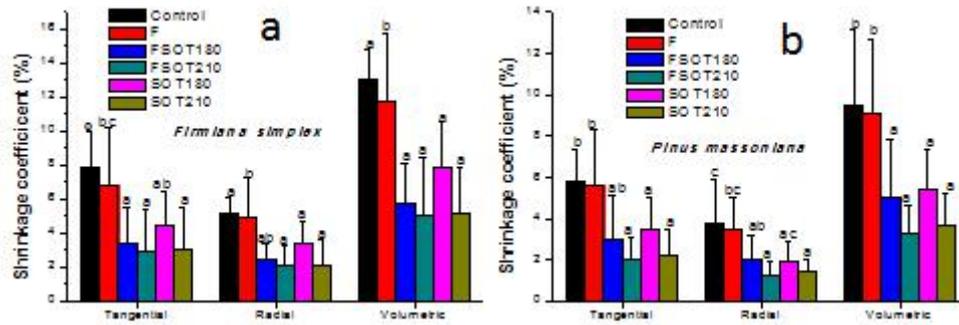
Figure 1. Shrinkage of control and freeze-silicone oil treated wood: (a) Firmiana simplex (b) Pinus massoniana.
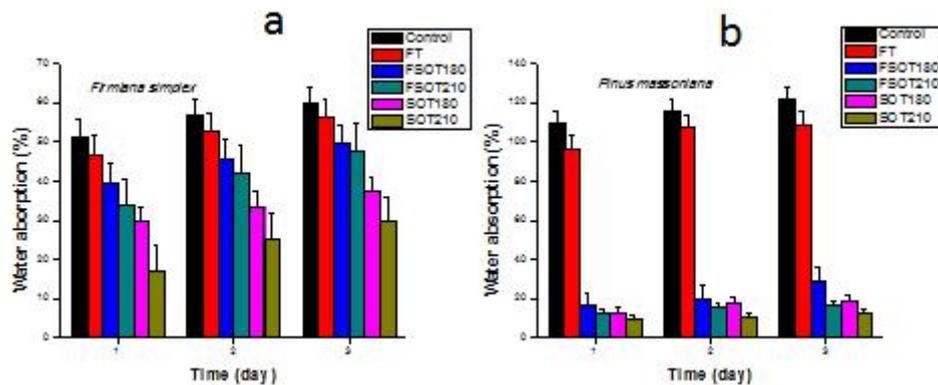

Figure 2. Water absorption of control and freeze-silicone oil treated wood: (a) Firmiana simplex (b) Pinus massoniana.

Figure 3 shows the FTIR spectra of control and freeze-silicone oil treated *F. simplex* and *P. massoniana* wood and Table 3 summarized the assignment of FTIR bands. The decrease in transmittance band at $3428cm^{-1}$ is related to hydroxyl functional groups (O-H stretching) from alcohols, phenols and acids in the treated woods present either in polysaccharides and lignin [4]. The present of O-H stretching is as a result of the alteration of cellulose crystallinity by dehydration [30,31]. The assignment of band at $2971cm^{-1}$ is connected to C–H widening [32], composed of overlapping asymmetric and symmetric stretch vibrations of $-CH_2-$ and $-CH_3$ as a result of relative changes in structural composition of the wood i.e changes in lignin methoxyl groups which lead to CH_3 stretching with lower CH stretching frequencies [30,31,33]. The assigned band at $1599 cm^{-1}$ was linked to lignin (aromatic skeletal C=C) and benzene ring stretching [34], thus resulting to increase in structural diversity around aromatic rings probably due to upsurge in lignin content [35,36,37] in the treated *F. simplex* and *P. massoniana* wood. The carbon-oxygen (C-O) stretching at $1259cm^{-1}$ is owed to carbonyl distortion in the ester bonds (lignin) and xylan (hemicelluloses) for the duration treatments. The spectra at $1057cm^{-1}$ corresponds to symmetric C-O-C dialkyl ethers and C-O ester stretching vibrations in methoxy groups, C-O distortion in cellulose and C-H deformation and β-O-4 linkages in lignin [36, 38, 39]. Band assigned at $896cm^{-1}$ is attributed to bending vibration in lignin (C-H out-of-plane) and β-glycosides in polysaccharides [34,36,38,39,40,41].

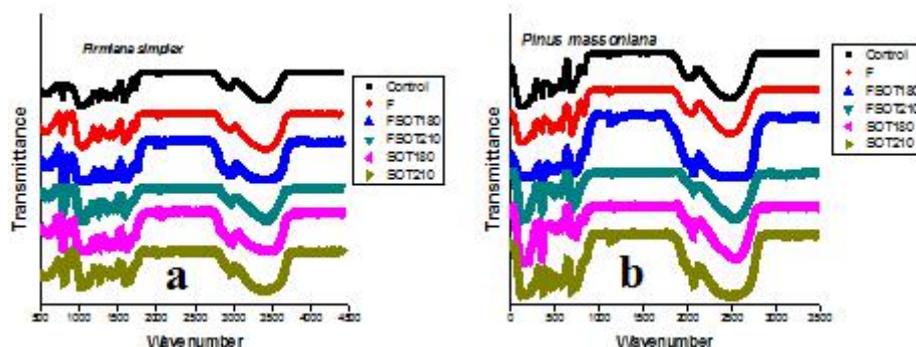***Figure 3.*** *FTIR spectra of control and freeze-silicone oil treated wood: (a) Firmiana simplex (b) Pinus massoniana.*

Table 3. *FTIR band assignment and description in Firmiana simplex and Pinus massoniana wood.*

Wave length cm^{-1}	Description and band assignment
3428	O-H stretching of water, alcohols, phenols, acids
2971	C–H stretching vibration in methyl and methlene groups [5]
1730	C-O stretching of carboxyl groups and acetyl groups in hemicellulose [42]
1599	C=C stretching of aromatic skeletal in lignin
1510	C=C stretching of aromatic skeletal in lignin [5]
1442	C-H deformation in lignin and xylan [39]
1421	C-H aromatic stretching in lignin and shuddering in carbohydrates [36]
1370	C-Hand OH stretching in methyl and phenol [42]
1333	C-H vibration in cellulose and C-O vibration in lignin [37]
1259	C-O stretching in lignin [42]
1233	C-O and C=O stretching in lignin and xylan [42]
1113	OH glucose ring stretching [36]
1057	C-O-C and C-O stretching of dialkyl ethers and methoxyl groups
896	C-H and β-glycosides vibration in lignin and polysaccharides [6]

Thermogravimetric analysis (TGA) of control and freeze-silicone oil treated *F. simplex* and *P. massoniana* wood are presented in Figure 4, indicating the thermal degradation of the wood components. First, second and third regions reflected the decomposition of extractives, cellulose and lignin contents in the wood [43]. The first region on the TGA curve was in the temperature between 100 - 284 °C, second region was between 278 - 384 °C and major thermal degradation occurred in this region while temperature in the third region was between 384 - 400°C. From the TGA curves, thermal degradation temperature of the wood occurred between 100 to 400 °C. Hemicelluloses degraded between 100 to 287 °C, cellulose degraded between 278 to 384 °C and lignin degraded between 91 to 400 °C. At higher temperature above 400 °C, the TGA curves indicated a descending slow continuous decomposition region (approaching zero, this showed that lignin was gradually degrading. Previous study opined that the thermal decomposition of hemicelluloses mainly decomposes at temperature between 200 to 315 °C, 315 to 400 °C for cellulose and 360-400 °C for lignin [44]. It should be noted that the decomposition of lignin occur over extensive temperature and there is a relative increase in lignin content with increase in thermal treatment temperature and time while invariably the relative cellulose content tend to decrease. Thermal decomposition of lignin span through a wide temperature as a

result of the present of propyl-benzene derivatives which gives it a strong chemical stability with slow reaction in comparison to cellulose and hemicelluloses [45].
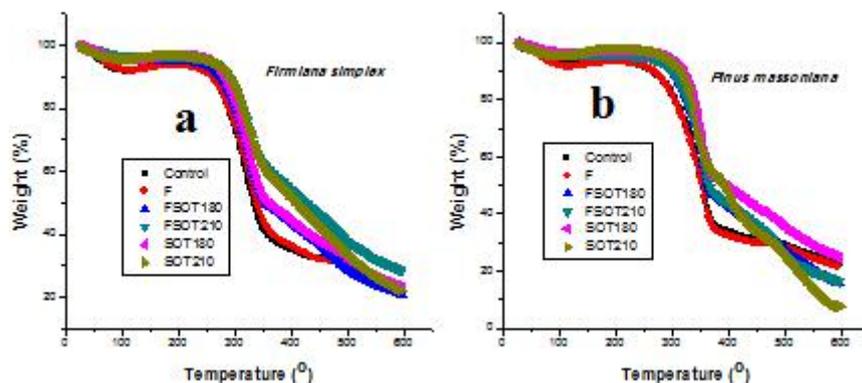

Figure 4. *TGA of control and freeze-silicone oil treated wood: (a) Firmiana simplex (b) Pinus massoniana.*

X-ray diffraction (XRD) of the control and freeze-silicone oil treated *F. simplex* and *P. massoniana* wood clearly show changes in the diffraction patterns (Figure 5). A typically diffractogram pattern which corresponds to cellulose I structure were identified at $(1\bar{1}0)$, (110), (200) and (040) with their corresponding diffraction angles (2θ) 12.10°, 16.00°, 22.24° and 34.62° [46]. Similar diffraction patterns were obtained with differences in the diffraction intensity only, due to changes in the wood biochemical component. The diffraction peaks at (200) were the most pronounced peaks with 22.24° corresponding to cellulose I crystalline structure [47] and the diffraction intensity at 34.6° was stable with no shift toward lower 2θ angle, suggesting that the glucan chains of cellulose were unaffected [47]. The treated wood samples showed high intensity compared to the control, indicating structural changes consequence upon the effect of the treatment. The crystallinity index (CrI) of *F. simplex* and *P. massoniana* wood increased from 16.66% to 17.86% and 12.5% to 68.42% after treatments and this agrees with previous studies [48,49,50]. The increase in relative crystallinity of the treated samples may be due to the degradation of cellulose and hemicelluloses in the amorphous regions, during thermal decomposition leading to unavailability of hydroxyl groups to water molecular [51] resulting in reduced hygroscopicity as reported above. Furthermore, previous works reported that subjecting wood to heat treatment could affect the accessibility of water by cellulose and microfibril bundles [4,52], because the microfibers in the crystalline structure of wood cellulose hinders the access of water to hydroxyl groups [4,53] and the rearrangement of paracrystalline regions of cellulose can increase the relative CrI of the wood [54].
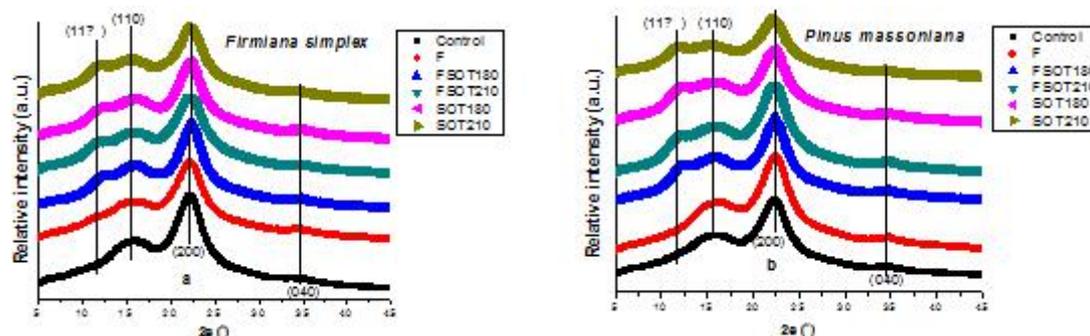

Figure 5. *X-ray diffraction of control and freeze-silicone oil treated wood: (a) Firmiana simplex (b) Pinus massoniana.*

4. Conclusion

The hygroscopic and chemical modification of two fast-growing woods treated using freeze-silicone oil treatments was experimentally studied in this work. *Firmiana simplex* and *Pinus massoniana* were the two wood species used and five experimental treatments (F, FSOT180, FSOT210, SOT180 and SOT210) were employed. The hygroscopic properties of the wood significantly decreased after the treatments, this confirms an increment in the hydrophobicity of the treated woods. The FTIR spectra showed changes occurred in the wood chemical constituents after treatments with regards hemicelluloses, cellulose and lignin degradation. TGA curves, indicated different stages of thermal degradation of the various wood components. Furthermore, XRD showed that the amorphous cellulose was affected in the treated wood, thus increased the cellulose crystallinity of treated wood. From this study, the use of freeze-silicone oil treatments in wood modification proved to reduce the hygroscopicity and modify the chemical components of evaluated wood species.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Author Contributions

Writing - original draft preparation: K.E.O.; Writing - review and editing: K.E.O., E,; A.I.; Conceptualization: K.E.O.; Methodology: K.E.O.; Software: K.E.O.; Q.A.; Validation: O.A.R.; Formal analysis: K.E.O.; E.A.I.; Investigation: K.E.O.; Resources: E.A.I.; Q.A.; Data Curation: K.E.O.; Visualization: K.E.O.; O.A.R.

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