Improved Interfacial Interaction between Wood and Styrene with the Help of Organically Modified Nanoclay

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Wood impregnated with styrene (ST) has a greater hydrophobicity than raw wood. Organically modified nanoclay can be used as a filler to increase the interfacial interaction between wood and ST. Raw wood shows an improved micro-structure, water uptake, modulus of rupture (MOR), modulus of elasticity (MOE), and thermal properties after impregnation with a mixture of i) non-branched organic ammonium-modified nanoclay (R-NH_3^+-clay) and ST; and ii) branched organic ammonium-modified nanoclay ($(R)_2N^+(CH_3)_2$-clay) and ST. Styrene with R-NH_3^+-clay-impregnated wood had a higher water uptake than the ST with $(R)_2N^+(CH_3)_2$-clay-impregnated wood. The MOE and MOR values of the ST with R-NH_3^+-clay-impregnated wood were higher than the ST with $(R)_2N^+(CH_3)_2$-clay-impregnated wood. Below 250 °C, the$(R)_2N^+(CH_3)_2$-clay with ST-impregnated wood had a greater thermal stability than the R-NH_3^+-clay with ST-impregnated wood.

Keywords: ST; Nanoclay; Morphological properties; Water uptake; Mechanical properties

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INTRODUCTION

Wood is widely used as a construction material because of its excellent mechanical properties and aesthetic appearance. However, it swells when it absorbs water from the environment, due to its –OH groups, and it shrinks when it dries. In the presence of water, wood is easily decomposed by fungi. Wood properties can be improved by well-chosen modifications, such as lumen modification, chemical modification, *etc.* (Matsuda 1992; Yasuda and Minato 1994; Rosca *et al*. 2003; Treu *et al.* 2003; Van Acker 2003; Epmeier *et al.* 2007; Dieste *et al.* 2008). Macromolecules generally cannot directly enter into a wood lumen. Though polymers are formed by *in situ* polymerization when many monomers, including styrene (ST) and methacrylate, enter wood, only the empty lumens in the wood are filled, which leads to a mixture of the two materials rather than a true composite. As a result, the products do not show the expected dimensional stability and water resistance expected of chemically modified wood.

Styrene-impregnated wood (IW) has been comprehensively studied and has demonstrated improved bending strengths, dimensional stabilities, compression values, and water resistances compared with wood that has under gone a soaking treatment (Loos and Robinson 1968; Hazer *et al.* 1993). The bending strength of ST-IW is lower than that of ST-glycidyl methacrylate-IW (Sultan *et al*. 2016). This is because glycidyl methacrylate works as a coupling agent between the wood and ST. Without using a coupling agent, however, the compatibility between wood and ST can be increased with the help of a nanofiller.

Past research has established that a small amount of nanofiller incorporated in a polymer matrix can remarkably enhance the physical, thermal, and mechanical properties, as wells as the biodegradation resistance compared with those of conventional virgin polymers (Lan *et al.* 1995; Gilman 1999; Dietsche *et al.* 2000; Byun *et al*. 2001; Kornmann *et al.* 2001; Su and Wilkie 2003; Deka and Maji 2013; Hazarika and Maji 2014; Wang *et al.* 2016). This is because the introduction of a nanofiller with a larger surface area into a matrix improves the compatibility between the nanofiller and matrix. However, the compatibility between hydrophilic nanoclay and hydrophobic polymers is poor. Therefore, wood impregnated with hydrophobic polymers and hydrophobic-modified nanoclay shows better wood properties than wood that is only impregnated with hydrophilic polymers (Cheng *et al.* 2000; Chang *et al.* 2003; Kornmann *et al.* 2005; Thostenson *et al.* 2005; Zhou *et al.* 2005; Bozkurt *et al*. 2007; Chandradass *et al.* 2007; Böger *et al.*2008).

The source of nanoclay is clay minerals, which are also called phyllosilicates. Phyllosilicates have a framework that is generated by a combination of tetrahedral and octahedral sheets. In a tetrahedral sheet, silica is the main component, whilst an octahedral sheet is comprised of diverse elements, such as Al, Mg, and Fe. Phyllosilicate 2:1 clays include smectite, mica, chlorite, and vermiculite. The smectite group can be further divided into nontronite, saponite, montmorillonite (MMT), and hectorite species (Bailey 1980; Moore and Reynolds 1997). The stacking of clay platelets leads to a Van der Waals gap or gallery between the platelets. It is possible to replace the cations in the alumina sheet with Mg^{2+} and Fe^{2+}cations. Replacement of $Al^{3+}$with divalent cations produces a negative charge on the layers. This negative charge can be balanced by alkali metal cations (Na^+, Li^+, or Ca^{2+}) positioned in the gallery between the alumino silicate layers and on the surface. When clay is hydrophobically modified, alkali metal cations on the clay surface are substituted with bulky alkyl cations.

Currently, several organoclays are available commercially at relatively low cost. Commercial organoclays include Cloister, Nanomer, Nanofil, and Synthetic fluoromica clays. Cloisters contain tallow and quaternary ammonium salt. In the Nanomer series, the MMT nanoclay surface is modified with primary alkyl ammonium and quaternary alkyl ammonium. These organoclays are commonly used as nanofillers in polymer matrices. Wood impregnated with a mixture of organic polymer and organically modified nanoclay have improved thermal, mechanical, and physical properties, and a greater resistance to biodegradation compared with wood impregnated with an organic polymer (Cai *et al*. 2007, 2008). The selection of an organoclay for the impregnation of a polymer matrix mainly depends on its chemistry.

In this study, the effects of the nanomers 1.30E, 1.31PS, 1.44P, and1.28E on a ST-wood system were studied. The effects of the nanomers were determined with physical, and mechanical properties; and morphological, and thermal analyses.

EXPERIMENTAL

Materials and Methods

Kumpang raw wood (RW) was obtained from the Forestry Department Sarawak, Malaysia. The nanoclays used in this study were Nanomer^{R}1.28E, Nanomer^{R}1.30E, Nanomer^{R}1.44P, and Nanomer^{R}1.31PS; all of the nanoclays were supplied by Sigma Aldrich (St. Louis MO, USA) and described in Table 1. The ST was supplied by A. S. Joshi and Company (Mumbai, India). Benzoyl peroxide was used as a free radical catalyst to induce polymerization of the ST. The chemical compositions of the fillers used to impregnate the RW are described in Table 2. The methods used in this work were obtained from Sultan *et al.* (2016) summarized below:

For the three-point bending test, the RW samples with the dimension of 300 mm (L) x 20 mm (T) x20 (R) mm have been impregnated with a mixture according to Table 2. The impregnations were conducted in a vacuum chamber of 75 mm (Hg) for 30 min and then the impregnated woods (IWs) were placed in an oven for 24 h at 105°C for polymerization to take place. The powder form of the RW and IWs was used to perform the Fourier transform infrared (FTIR) spectroscopic and thermogravimetric analysis (TGA). Fractured surfaces of the IWs were gold coated to investigate their interfacial bonding with the help of scanning electron microscope (SEM) test. The FTIR, SEM, and MOR analysis were conducted using a Shimadzu FT-IR 81001 spectrophotometer (Shimadzu; Kyoto, Japan), a Hitachi TM3030 JEOL (Tokyo; Japan), and a Shimadzu MSC-5/500 universal testing machine (Kyoto; Japan), respectively. Thermogravimetric analysis (TGA) was performed using a thermal analyzer (Model SDT Q600, TA Instruments; Tokyo, Japan).

Table 1. Description of the Modified Nanoclays

Name of the modified nanoclay	Amount and name of organic modifier used in Montmorillonite clay
Nanomer^R 1.28E	25 to 30 wt. % trimethyl stearyl ammonium
Nanomer^R 1.30E	25 to 30 wt. % octadecylamine
Nanomer^R 1.44P	35 to 45 wt. % dimethyl dialkyl (C14-C18) amine
Nanomer^R 1.31PS	0.5 to 5 wt. % aminopropyltriethoxysilane, 15 to 35 wt. % octadecylamine

Table 2. Amount of ST and Nanoclay for the Impregnation of the RW

Amount of Corresponding Materials for Impregnation of the RW					Name of the Impregnated wood (IW) Samples
ST (mL)	Nanomer^R 1.28E (g)	Nanomer^R 1.30E (g)	Nanomer^R 1.44P (g)	Nanomer^R 1.31PS (g)	
1000	10	-	-	-	ST-clay1.28-IW
1000	-	10	-	-	ST-clay1.30- IW
1000	-	-	10	-	ST-clay1.44-IW
1000	-	-	-	10	ST-clay1.31-IW
1000	-	-	-	-	ST-IW

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy Analysis

The Fourier transform infrared (FTIR) spectra of the wood impregnated with ST, ST-clay1.44, ST-clay1.28, ST-clay1.30, and ST-clay1.31 are shown in Fig. 1. The peaks from 4000 $cm^{-1}$to 3000 cm^{-1} and from 2900 cm^{-1} to 2800 cm^{-1} corresponded to the stretching vibrations of H-bonds in -OH groups and C-H bonds in methyl and methylene groups, respectively (Sultan *et al*. 2017). The intensity of the peak from 4000 cm^{-1} to 3000 cm^{-1} for the–OH of ST-clay1.28-IW was smaller compared with that of the RW, whereas the ST-clay1.44-IW, ST-clay1.30-IW, ST-clay1.31-IW, ST-IW, and RW showed similar peak intensities around that area. To explain this, it is hypothesized that the polarity of the –OH groups in the wood was reduced by only clay1.28. The peak intensities of the –OH groups of the nanocomposites and composites were produced by wood and nanoclay because all of the samples were fully dried at temperatures up to 105 °C before FTIR analysis. The peak at 698 cm^{-1} is characteristic of bending vibrations of $Mg(OH)_2$, Fe–O, and Al-O-Si, and out-of-plane bending of -OH in wood (Kondoand Sawatari 1996; Madejova 2003).

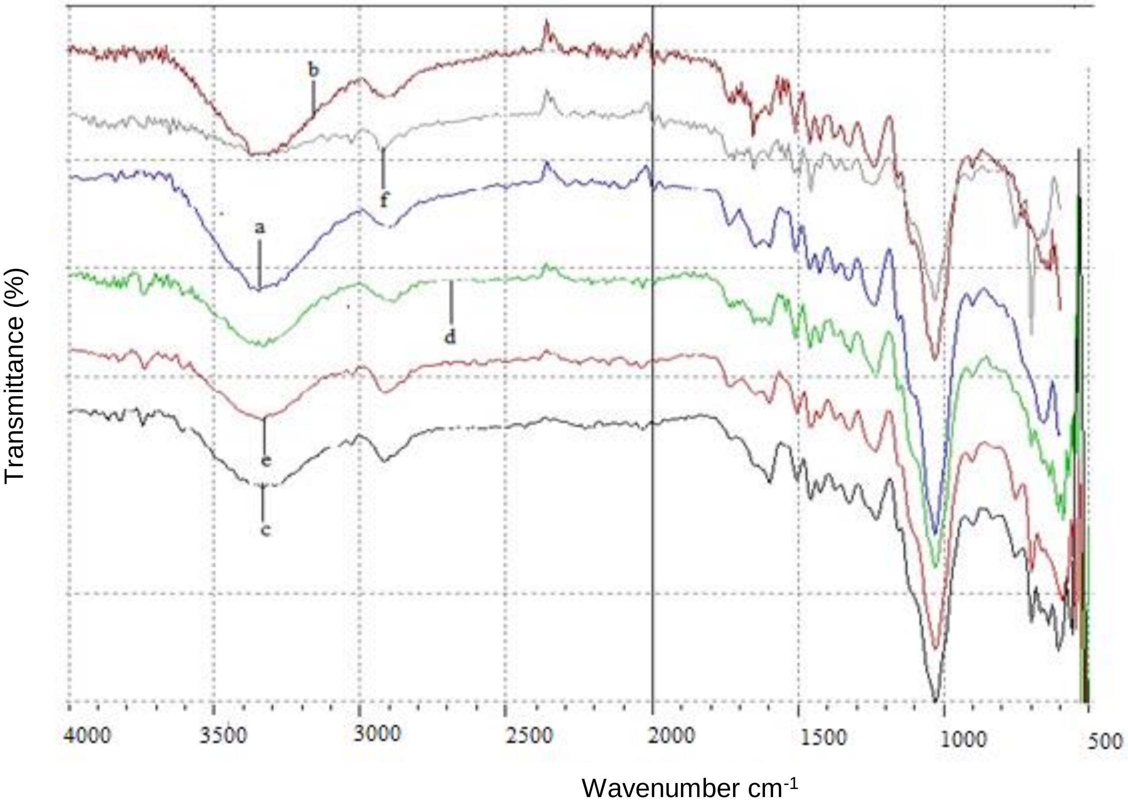

Fig. 1. FTIR spectra of the a) RW, b) ST-IW, c) ST-Clay1.30-IW, d) ST-clay1.31-IW, e) ST-clay1.44-IW, and f) ST-clay1.28-IW

Every IW sample showed a peak at 698 cm^{-1}, except for the RW. The intensity of this band was the highest for the ST-clay1.28-IW, followed by the ST-clay1.44-IW, ST-clay1.30-IW, and ST-clay1.31-IW. This order corresponded with the weight percentage gain (WPG) values for each sample. The C-H bending vibration peak at 750 cm^{-1} for ST-clay1.44-IW, ST-clay1.30-IW, and ST-clay1.28-IW were observed, whereas this peak was absent in the case of ST-IW. This is because the π electron of ST was polarized by Al^{3+} in ST-clay-IW samples (Yao *et al.* 2013). The stretching of C-H in the methylene and methyl groups of the RW, ST-clay1.31-IW, and ST-IW occurred at 2897 cm^{-1}, and the C-H stretching of those groups shifted to 2907 cm^{-1}, 2916 cm^{-1}, and 2924 cm^{-1} for ST-clay1.30-IW, ST-clay1.44-IW, and ST-clay1.28-IW, respectively. This result demonstrated that there was a chemical interaction between the wood and ST with clay1.30, clay1.28, andclay1.44, which was reflected in the modulus of rupture (MOR) results. In general, organic molecules can enter into the Van der Waals gap between clays by interacting with the clay surface *via* dipole-dipole, ion-dipole, and hydrogen bonding (Vaia *et al.*1994; Ho *et al.* 2003; Choi *et al.* 2004). Thus, in the FTIR results of the nanoclay-IW samples, there were many groups whose peaks and positions had shifted compared with those of the RW. Thus, there was a chemical interaction between the wood, nanoclay, and ST.

Scanning Electron Microscopic Analysis

Scanning electron micrographs of the RW and IWs are shown in Fig. 2.

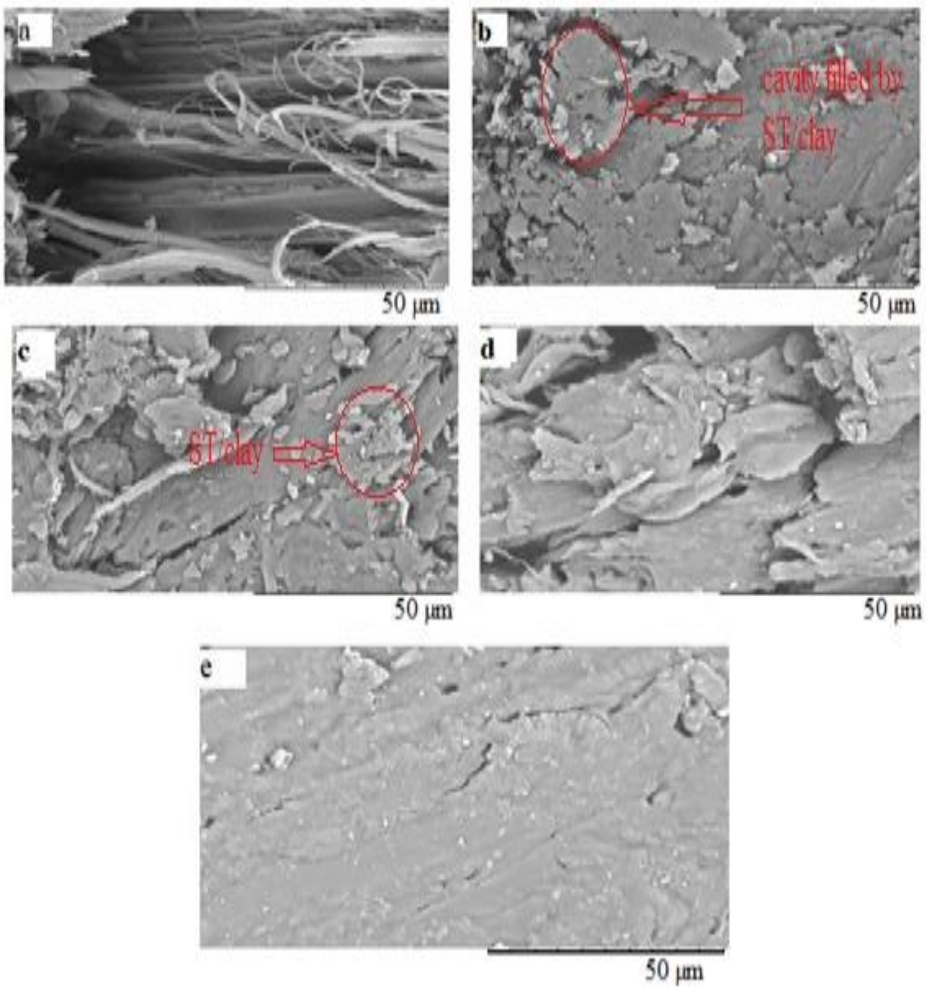

Fig. 2. SEM micrographs of the (a) RW, (b) ST-clay1.44-IW, (c) ST-clay1.30-IW, (d) ST-clay1.31-IW, and (e) ST-clay1.28-IW; the images were obtained at 1500×magnification

It was observed that the lumen and tracheids of the wood were filled with the solid ST polymer and nanoclay. The surface of Fig. 2e was smoother than those shown in Figs. 2b, 2c, and 2d. This was because the WPG (Table 3) of the RW after impregnation with the ST-clay1.28 was higher than that of the RW impregnated with ST-clay1.30, ST-clay1.31, and ST-clay 1.44. Also, Figs.2b, 2c, 2d, and 2e show that the compatibility of the wood, ST, and clay1.31 was lower than that of the wood, ST, and clay1.44, and the wood, ST, and clay1.28. Thus, ST-clay1.31-IW had the lowest MOR value compared with that of theST-clay1.44-IW, ST-clay1.30-IW, and ST-clay1.28-IW.

Weight Percentage Gain (WPG) and Water Uptake (WU)

Both the WPG and water uptake (WU) values are shown in Table 3. It was clear that the weight gain in the RW impregnated with ST-clay mixtures was higher than that of the RW impregnated with ST. A possible explanation for this is that the organically modified nanoclay contains larger alkyl groups with quaternary ammonium ions or a primary amine with a larger alkyl group. The penetration capability of the charged part of the quaternary ammonium ion or primary amine group into polar organic materials is higher than that of ST into polar organic materials. The compatibility between the ST molecule and an alkyl group of a quaternary ammonium ion or primary ammonium group located on the surface of the nanoclay and between galleries of nanoclay is favorable. When wood is immersed in a mixture of ST-organically modified nanoclay, both the ST and nanoclay enter the wood because the ST adsorbs on to the nanoclay surface and enters the nanoclay galleries. The WPG of the RW impregnated with ST-clay1.30 and ST-clay1.31 was lower than that of the RW impregnated with ST-clay1.44 and ST-clay1.28. A possible explanation for this is that the absorption capability of the ST on the alkyl part of a primary ammonium ion ($R\text{-}NH_3^+$) on the clay is lower than that of the ST on the alkyl part of a quaternary ammonium ion ($(CH_3)_2N^+(R)_2$). As a result, the ST-clay1.44 and ST-clay1.28 were able to penetrate the RW easier compared with ST-clay1.30 and ST-clay1.31. Wood properties, such as the WU and biodegradation of modified wood, depend on what degree the RW is impregnated and the functionality of the filler in the wood.

The void area on the wood surface facilitates water penetration into the wood cell walls with hydrophilic hydroxyl groups. The RW and ST-IW showed a higher percentage of water absorption compared with each ST-clay-IW. This is because the WPG of the RW impregnated with ST was lower than that of the RW impregnated with ST-clay. As a result, more void space was present in the ST-IW than in the ST-clay-IWs. The hydrophilic properties of the ST-clay1.44 and ST-clay1.28 were lower than of the ST-clay1.30 and ST-clay1.31 because the hydration degree of the cations and anions were higher than that of the polar ions and their steric hindrance impeded the entrance of water molecules. The ST-clay1.44-IW showed more hydrophilic properties than the ST-clay1.28-IW because of the WPG of the RW.

Table 3. WPG by Impregnated Materials in RW, and WU of the RW and IWs

Impregnated materials in RW	WPG	Sample	WU(%)
ST	1.28	RW	80± 10.150
		ST-IW	70± 8.33
ST-clay1.30	13.75	ST-clay1.30-IW	38± 4.15
ST-clay1.31	9.58	ST-clay1.31-IW	45±8.25
ST-clay1.44	23.3	ST-clay1.44-IW	30± 6.30
ST-clay1.28	30.57	ST-clay1.28-IW	2± 0.31

Values represent the means of five replicates; while the± values represent the standard deviation.

Modulus of Rupture and Modulus of Elasticity

The modulus of elasticity (MOE) and MOR values of the RW, ST-IW, and ST-clay-IW materials are given in Table 4. The table shows that the composites exhibited higher MOE and MOR values than the RW. This was attributed to the presence of fillers that exerted Van der Waals forces within the wood cell walls. Among the IWs, the MOE and MOR values were the highest for the ST-clay1.30-IW because $R\text{-}NH_3^+$ was on the surface of clay1.30 (Benítez *et al.* 2011). The inter-ionic force between the –OH group of the wood and $R\text{-}NH_3^+$ is higher than that of the–OH group of the wood and $(R)_4N^+$ because the cationic charge on the nitrogen is screened by an alkyl group (Fornes *et al.*2003). Therefore, the RW bonded more with the ST-clay1.30 than ST-clay1.44. Similarly, it was expected that the MOR value of the ST-clay1.28-IW would be higher than of the ST-clay1.44-IW, but the reverse was true. It has been reported that a nanocomposite with one-tailed ammonium ($R\text{-}NH_3^+$) clay is less effective than that with two-tailed ammonium ($(R)_2\text{–}N^+(CH_3)_2$) clay (Hotta and Paul 2004). Thus, it was expected that the penetration of clay1.44 into the ST-wood system would be higher than that of clay1.28. Among the ST-clay-IW samples, the ST-clay1.31-IW showed the lowest MOE and MOR values. This was because the nanoclay was modified by a mixture of octadecyl amine and triethoxy amino alkyl silane. The penetration of triethoxy amino alkyl silane into the wood was not easy because the silane group is not stress-free, which is caused by its bulkiness. The silane group broke the hydrogen bonds of the wood.

Table 4. MOE and MOR of the RW and IWs

Sample	MOE (GPa)	MOR (MPa)
RW	6.29±2.45	55.21±8.45
ST-IW	13.25±3.10	84.71±5.31
ST-clay1.30-IW	19.48±2.11	153.18±8.34
ST-clay1.31-IW	6.64±1.21	64.87±4.51
ST-clay1.44-IW	13.29±2.12	100.56±9.25
ST-clay1.28-IW	12.56±1.44	95.42±4.43

Values represent the means of five replicates; while the ± values represent the standard deviation

Thermogravimetric Analysis

The TGA results of the RW and ST-clay-IWs are shown in Fig. 4, and the corresponding thermal characteristics are given in Table 5.

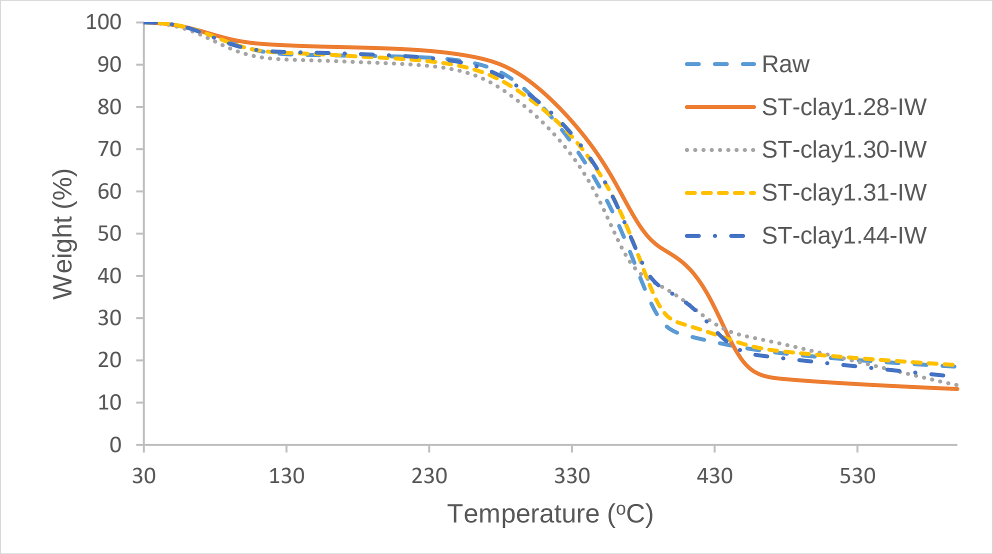

Fig. 4. TGA of the RW, ST-clay1.30-IW, ST-clay1.31-IW, ST-clay1.44-IW, and ST-clay1.28-IW

Figure 4 shows that the RW had two stages of thermal degradation, whereas all of the ST-clay-IWs had three stages. The first stage of weight loss occurred from 40 °C to 110 °C because of the evaporation of moisture from all of the samples (Liu *et al.* 2013). The initial weight loss of the samples below 110 °C was the highest for the ST-clay1.30-IW, lowest for the ST-clay1.28-IW, and similar for the ST-clay1.31-IW, ST-clay1.44-IW, and RW. This was because the hydrophilicity of R-$NH_3^+$was greater than that of $(R)_2N^+(CH_3)_2$; the RW was impregnated to a higher degree with theST-clay1.28 than with the ST-clay1.31.

Between 120 °C and 320 °C, the decomposition rate of theST-clay1.31-IW was higher than that of the ST-clay1.28-IW, ST-clay1.30-IW, ST-clay1.44-IW, and RW. This was because (3-aminopropyl) triethoxysilane boils at 217 °C. The third stage of decomposition of theST-clay-IWs occurred from 392 °C to 462 °C. In this third thermal degradation stage, the cellulose and lignin were degraded (Kim *et al.* 2006; Yang *et al.* 2007). The weight loss rate of the ST-clay-IWs was lower than that of the RW. This was because the nanoclay did not decompose in this temperature range. Well-distributed clay layers could prevent the passage of volatile decomposition products through the composite during TGA (García *et al.* 2009; Sanchez-Jimenez *et al.* 2012). It could be hypothesized that among the clays the clay1.28 was more dispersed into wood.

Table 5. TGA of the Samples

Sample	Transition	Transition Temperature			Weight Loss at Corresponding Transition (%)	Residual Weight (%) at Last Stage Transition
		T_i(°C)	T_m(°C)	T_f(°C)		
RW	1st	37.8	80.36	121.7	7.30	24.81
	2nd	127.58	354.51	425.59	67.65	
ST-clay1.30-IW	1st	40.04	80.04	120.33	9	16.59
	2nd	220.27	360.07	380.21	63.46	
	3rd	390.00	420	450.20	12	
ST-clay1.44-IW	1st	43.7	81.15	120.22	7.20	20.00
	2nd	129.65	375.83	390.42	58.00	
	3rd	396.34	425.27	459.34	15.00	
ST-clay1.28-IW	1st	43.7	74.15	112.22	4.83	15.22
	2nd	129.65	343.83	387.42	45.92	
	3rd	396.34	434.27	494.34	31.03	
ST-clay1.31-IW	1st	40.00	79	126.00	7.30	20.00
	2nd	240.00	380	420.00	63.00	
	3rd	420.00	440	480.00	10.70	

T_i: onset temperature; T_m: temperature corresponding to the maximum mass loss rate; and T_f: end temperature

CONCLUSIONS

1. The impregnation of the Kumpang raw wood (RW) with styrene (ST) and clay was verified from the FTIR, SEM, and WPG results.
2. The RW and ST-IW showed higher percentages of water absorption than the ST-clay-IWs. The hydrophilic property of theST-clay1.44 and ST-clay1.28 was lower than that of the ST-clay1.30 and ST-clay1.31 because the hydration degree of the cations and anions were higher than that of the polar ions and the steric hindrance of the organically modified nanoclay impeded the entrance of water molecules.
3. The modulus of elasticity (MOE) and modulus of rupture (MOR) values were the highest for the ST-clay1.30-IW and this is consistent with the idea that the non-branched organic ammonium-modified nanoclay created more electrostatic forces with the wood than the branched organic ammonium-modified nanoclay (clay1.31).
4. The ST-clay1.28-IW showed the highest thermal stability among the samples used in this study.

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