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A novel application of silicone-based flame-retardant adhesive in plywood

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Abstract

A silicone-based elastomer filled with vinyl-silane treated aluminum hydroxide was used to replace conventional polyurethane-based adhesive to provide a flame-retardant adhesive for plywood. The shear strength and fire performance of such a silicone-based (SI) adhesive glued plywood (SI/plywood) were investigated and compared to those of the polyurethane-based (PU) adhesive glued plywood (PU/plywood). The shear strength of the SI/plywood [(0.92 ± 0.09) MPa] was about 63% lower than that of the PU/plywood at room temperature, but it was less sensitive to water (62% reduction for the PU/plywood and 30% reduction for the SI/plywood after hot-water immersion at 63 °C for 3 h). The fire performance of plywood was assessed by a simulated match-flame ignition test (Mydrin test), lateral ignition and flame spread test, cone calorimetry, and thermocouple measurements. With a higher burn-through resistance and thermal barrier efficiency, and lower flame spread and heat release rate, the SI/plywood exhibited a superior fire-resistance and reaction-to-fire performance and improved fire-resistance as compared to the PU/plywood. The SI adhesive generated an inorganic protective layer on the sample surface that visibly suppressed glowing and smoldering of the plywood during combustion. The SI adhesive was also combined and reinforced with cellulosic fabric (CF) or glass fabric (GF) to prepare composite plywood (SI/CF/plywood and SI/GF/plywood) with improved fire performance. The cone calorimetry and thermocouple measurements indicated that the use of CF or GF in SI/CF/plywood and SI/GF/plywood, respectively, suppressed the delamination and cracking of the composite plywood and promoted the formation of an effective thermal barrier during smoldering and

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Conflict of interest
None.

flaming combustion. Particularly, the SI/GF/plywood exhibited the most effective fire barrier with no crack formation, and the lowest heat release rate among the plywood types investigated in this study.

Keywords

Flame-retardant adhesive; Silicone-based adhesive; Plywood; Shear strength; Fire performance; Thermal barrier

1. Introduction

Wood-based products such as plywood, fiberboard, particleboard, laminated veneer lumber, and wood-plastic composites, provide a substitute for solid wood while retaining the requisite structural properties with favorable performance and low cost. They have been widely used in residential, commercial, and industrial buildings [1,2]. In North America, most residential housing and a significant portion of low-rise construction are built using wood-based products [3]. Meanwhile, mid-rise (6 stories) and high-rise (12 stories) timber constructions are becoming more common [4,5]. The replacement of non-flammable materials (e.g., concrete and steel) with wood-based products, which are intrinsically flammable, increases the fire load and fire hazard for these buildings. Therefore, there has been a surge in research in North America focused on assessing and improving the performance of wood-based products in structural fires [6–12], which is resulting in undated standards for the fire performance of engineered timber products specifically to address delamination [13].

Two key aspects of fire performance are fire-resistance and reaction-to-fire [14]. Fire-resistance refers to the ability of a material or system to withstand exposure to high temperatures based on thermal insulation and mechanical integrity evaluations. Reaction-to-fire defines how a material or system will contribute to fire development and refers to measurements including ignitability, energy released by combustion, and flame spread. Delamination in engineered timber drastically deteriorates fire-resistance and reaction-to-fire of the wood product. It directly affects the structural integrity of the product (due to the failure of the adhesive) and induces an increase in flame spread and heat release rate (due to the detachment of superficial charred insulating layer and consequent exposure of the virgin underlying material to direct flame impingement).

Three methods are commonly employed to provide wood-based products with improved fire-resistance and reaction-to-fire: chemical impregnation [2,15–18], incorporation of flame retardants into the adhesive [19–22], and flame-retardant coatings [23–27]. For chemical impregnation, the most widely used flame-retardant chemicals for treating wood-based products are inorganic salts that contain elemental phosphorus or boron. However, phosphates usually pose an adverse effect on the mechanical properties of wood products. Moreover, phosphates easily leach out due to their poor water resistance [18,28]. Boron compounds are not recommended due to their hygroscopicity that might affect the dimensional stability of wood [29,30]. Meanwhile, these chemicals could also leach out and be harmful to the environment and human health [31]. For the second method, the

incorporation of flame retardants inevitably increases the viscosity and curing time, and decreases the bond strength of the adhesive [21]. Flame-retardant coatings, particularly intumescent coatings, are a convenient and effective way to decrease the flammability of the substrate materials, but they can be affected by aging and mechanical abrasion/impact [23,27]. Coatings also affect the aesthetics and appearance of wood. Therefore, there is a need for flame-retardant technologies for wood-based products that are durable, effective, environmentally friendly and preserve the wood aesthetics.

Silicones have been successfully used in the field of flame retardancy. Thanks to their high thermal stability, minimal sensitivity to external heat flux, low heat release rate, and low toxic gas generation during combustion [32–34]. Bourbigot et al. [35] used a phenyl-branched silicone coating as a thermal barrier on the backside of steel. They found that the silicone-based coating performed an effective fire barrier. The backside temperature of the coating protected steel was 130 °C lower than that of the non-protected steel in a fire-resistance test (the coating was exposed to an open flame around 1100 °C). They also reported that the chain length and crosslinking density of the silicone-based coatings affected their thermal stability and barrier performance (i.e., ability to prevent burn-through and thermally shield the substrate) [36]. Our previous research [37] showed that a silicone-based backcoating drastically increased the fire performance of the cellulosic fabrics. The backcoating imparted the cellulosic fabrics with an advantageous combination of flaming/smoldering ignition resistance without affecting the original color and general appearance of the fabric's face. Silicone-based polymers can be used as adhesives and exhibit high flexibility, wetting capability, excellent chemical and weathering resistance, a relatively low curing temperature, and a benign toxicological profile [38–41]. More importantly, silicone-based adhesives are expected to be beneficial in terms of delamination resistance in wood engineered products due to their high thermal stability and high yield of inorganic thermally stable residue [42].

In this work, we investigate the use of a silicone-based elastomer filled with vinyl-silane treated aluminum hydroxide to increase delamination resistance and fire performance of plywood. The shear strength and fire performance of such a silicone-based adhesive glued plywood were investigated and compared to those of a conventional polyurethane-based adhesive glued plywood. The use of cellulosic or glass fabrics was also explored to further improve the fire performance of the resulting composite plywood.

2. Materials and methodsⁱ

2.1. Materials

All materials were used as received unless otherwise indicated. A two-component (a base and a curing agent) silicone-based elastomer crosslinked by platinum-catalyzed

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hydrosilation (Sylgard 184) was purchased from Dow Corning (USA). A vinyl-silane modified aluminum hydroxide (VSATH) (Apyral 40 VS1) was provided by Nabaltec AG (Germany). A conventional ethyl acetate (Analytical reagent) was obtained from Macron Fine Chemicals (USA). The one-component polyurethane-based adhesive (Original type) for wood was purchased from Titebond (USA). The wood used in this work was scroll saw veneer sheets of aspen [*Populus grandidentata*, 1.6 mm thick, density of (0.526 ± 0.002) g/cm³] and purchased from Ocooch Hardwoods (USA). The cellulosic fabric (CF) was 100% cotton [white plain weave of $(19 - 33)$ threads/cm², with an areal density of (115 ± 1) g/m²]. The glass fabric (GF) was Style 104 [ECD 900 1/0, with an areal density of (19.0 ± 0.1) g/m²] and supplied by Hexcel (USA).

2.2. Sample preparation

VSATH (20.43 g) was dispersed in Sylgard 184 base (10 g) and ethyl acetate (10 g) for 5 min by using a bladeless mixer (SpeedMixer, Flack Tek Inc, USA) at 2500 rotations/min. Then the curing agent (1 g) was added and mixed for another 1 min. The resulting silicone-based (SI) adhesive was applied by brush to both sides of a veneer specimen. Then, the adhesive-coated wood veneer was stacked between two uncoated wood veneers with the grain directions of two adjacent veneers perpendicular to each other (Fig. 1a). For the composite plywood containing CF (SI/CF/plywood) or the composite plywood containing GF (SI/GF/plywood), the CF or GF were used in combination with the SI adhesive (Fig. 1b). A single fabric layer was placed between two adjacent veneer layers. The adhesive was applied by brush to the veneer above and underneath the fabric. All the SI adhesive glued samples were prepared in accordance with such a methodology followed by hot-pressing (M-12-1, Grimco, USA) at 120 °C for 2 h with a pressure of 5 MPa. Complete evaporation of acetate occurred during curing and lead to a final content of VSATH in the SI adhesive of 65% by mass.

Samples glued by the conventional polyurethane-based (PU) adhesive were prepared with the same protocol, but the hot-pressing was performed at 80 °C. Before hot pressing, the mass ratio between adhesive and wood veneer in the PU adhesive and SI adhesive glued plywood samples was (20 ± 1) % and (60 ± 1) %, respectively (Table 1). Some adhesive was removed during the hot pressing and, as a result, the content of adhesive in the plywood decreased. The final plywood composition and the adhesive to wood mass ratio (after hot pressing) for all the plywood types are shown in Table 1. The presence of CF or GF did not significantly affect the content of adhesive in the samples after hot pressing.

2.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the adhesives were collected in attenuated total reflection mode using a Tensor 27 FTIR spectrophotometer (Bruker). Spectra were signal averaged over 128 scans at a resolution of 4 cm⁻¹ in the $(4000 - 600)$ cm⁻¹ wavenumber region.

2.4. Thermogravimetric analyses (TGA)

TGA curves of the adhesives were recorded using a Q 600 TGA analyzer (TA Instruments, USA) under a 50 mL/min ultra-high purity nitrogen flow rate from room temperature (RT) to 800 °C at a heating rate of 10 °C/min. Before test, the samples were oven-dried at 60 °C

for 24 h to obtain the constant weight. Three replicates (about 15 mg each) were tested and the standard deviations (SDs) were calculated for each adhesive formulation.

2.5. Shear strength test

The shear strength of the plywood samples was determined using a universal test machine (Model 45, MTS, USA) in accordance with ASTM D906–98 [43]. The dry and wet shear strength of the plywood samples was measured before and after immersion in water, respectively. For the dry shear strength test, the specimens were conditioned at a relative humidity of $(50 \pm 2) \%$ and $(22 \pm 2) ^\circ\text{C}$ for three days. For the wet shear strength test, the specimens were submerged in deionized water at RT for 24 h or $63 ^\circ\text{C}$ for 3 h. Then, they were air-dried at RT for 10 min before testing. The speed of crosshead was 2.0 mm/min for all the tests. Six replicates (threeply, $25.4 \text{ mm} \times 82.6 \text{ mm}$, gluing area of $25.4 \text{ mm} \times 25.4 \text{ mm}$) were tested and SDs were calculated for each plywood type. The shear strength values were calculated as follows:

$$\text{Shear strength (MPa)} = \frac{\text{Tension force (N)}}{\text{Gluing area (mm}^2\text{)}}$$

2.6. Fire performance

2.6.1. Mydrin test—The Mydrin test [44] is a simulated match-flame ignition test that uses a butane burner compliant with a British Standard (BS 5438) [45] and was originally developed for upholstery furniture materials. Here, we used plywood samples (three-ply, $220 \text{ mm} \times 100 \text{ mm}$) mounted on a vertical rig, as shown in Fig. 2. The butane burner flame impinged on the samples throughout the duration of the test. The four edges of the sample were covered by an aluminum tape. With the burner in the vertical orientation, the height of the flame was set to $(45 \pm 2) \text{ mm}$. With the burner tube in the horizontal position, the horizontal flame extension length decreased to $(23 \pm 2) \text{ mm}$. The horizontal distance from the end of the burner to the face of the sample was $(17 \pm 1) \text{ mm}$. The camera was used to record the whole testing process. The time to burn-through was recorded to assess the fire-resistance of the plywood samples.

2.6.2. Lateral ignition and flame spread test (LIFT)—A LIFT testing apparatus [46] was used to study auto-ignition and flame propagation of the plywood. The specimens (five-ply, $300 \text{ mm} \times 100 \text{ mm}$) were mounted in a custom-made ceramic frame. The ceramic frame was built with two layers of 12 mm thick thermal ceramic board. It was designed to fit in the LIFT apparatus and insulate the edge of the samples (Fig. 3, top). The frame was positioned in the LIFT apparatus such that the incident radiant heat flux (q''_{incident}) varied from approximately 44 kW/m^2 to 10 kW/m^2 (with an expanded total uncertainty of $\pm 5\%$ of the reading assuming a coverage factor of 2) from left to right along the specimen (Fig. 3, bottom). No pilot flame was used to aid ignition of the specimen, and the incident heat flux was held constant for the duration of the test. Once the radiant panel had achieved a steady state heat flux, the frame holding the specimen was rapidly inserted into the apparatus and the test began. After the desired duration had been achieved, the specimen was rapidly removed from the apparatus to end the test. Two replicates were tested for the SI/plywood

and the PU/plywood. Here, the LIFT test was mainly used to evaluate ignitability and char integrity of the tested materials.

2.6.3. Cone calorimetry—A cone calorimeter was used to measure ignitability, mass loss rate and heat release rate in accordance with ASTM E1354–17 [47]. A standard metal frame was used to protect sample edges and minimize warping. All the specimens (three-ply, 100 mm × 100 mm) were placed in an aluminum foil pan (100 mm × 100 mm × 5 mm) before being tested at a set exposed heat flux of 35 kW/m² in horizontal configuration. Three replicates were tested and SDs were calculated for each plywood type.

2.6.4. Thermocouple measurements—Cone calorimetry was also used to evaluate the effect of the adhesive on delamination and fire-resistance. Three thermocouples (K-type, KMQXL-020G-12, Omega Engineering Inc.) were installed on the backside of the plywood with aluminum adhesive tape (see Fig. 4). Each thermocouple measured the temperature at about 2 mm from the center of the backside, and was connected to a wireless transmitter (installed on the bottom holder) (MWTC-D-K-915, Omega Engineering Inc.). A wireless receiver (MWTC-REC5–915, Omega Engineering) was used to log the thermocouple data. Dynamic temperature measurement was recorded at a sampling interval of 1 s during the cone calorimetry test. Three replicate tests were run for each plywood type for a total of nine measurements per plywood type. The SDs were calculated.

2.7. Scanning electron microscopy (SEM)-Energy dispersive spectroscopy (EDS)

The surface morphology of the combustion residue was investigated by a field emission Ultra 60 SEM analyzer (Zeiss, USA) with an acceleration voltage of 3 kV. EDS spectra were collected on selected areas (5 μm × 5 μm) at 10 kV acceleration voltage. All the samples were sputter-coated with 4 nm of platinum layer prior to SEM imaging.

3. Results and discussion

3.1. FTIR spectra of the adhesives

Fig. 5 shows the FTIR spectra of the polyurethane-based (PU) adhesive and the silicone-based (SI) adhesive investigated in this study. The spectrum of the PU adhesive showed the characteristic polyurethane absorption peaks at 3336 cm⁻¹ (N–H stretching), 2939 cm⁻¹ (C–H stretching), and 1730 cm⁻¹ (C=O stretching) [48,49]. For the spectrum of the SI adhesive, the absorption peaks at 2963 cm⁻¹, 1259 cm⁻¹, 1009 cm⁻¹, 789 cm⁻¹ and 727 cm⁻¹ were attributed to the C–H stretching, C–H bending, Si–O–Si stretching, and Si–CH₃ bond, respectively [37].

3.2. Thermal degradation behavior of the adhesives

The TGA and derivative thermogravimetry (DTG) curves of the adhesives in inert atmosphere are shown in Fig. 6a and 6b, respectively. The related data are listed in Table 2. Both formulations showed two main degradation steps (DSs). The temperatures at which the DTG peak occurred for the first DS and the second DS are indicated as T_{max1} and T_{max2} , respectively. The mass loss rates measured at T_{max1} and T_{max2} are indicated as MLR_{max1} and MLR_{max2} , respectively. For the PU adhesive, T_{max1} and T_{max2} were (325 ± 1) °C and

(451 ± 1) °C, respectively, and only (5 ± 2) % by mass residue was left at 800 °C. Comparatively, the SI adhesive showed a lower T_{max1} [(285 ± 2) °C], a higher T_{max2} [(458 ± 1) °C], and a much higher residue [(60 ± 1) % by mass] at 800 °C. Meanwhile, MLR_{max1} and MLR_{max2} of the SI adhesive were only (0.35 ± 0.03) %/°C and (0.15 ± 0.01) %/°C, which were 75% and 52% lower than those of the PU adhesive [(1.42 ± 0.03) %/°C and (0.31 ± 0.01) %/°C], respectively. The values of MLR and residue suggested a far superior fire performance of the SI adhesive as compared to the PU adhesive.

3.3. Shear strength test

Shear strength is a key parameter for adhesives. In this work, dry shear strengths (before water immersion) and wet shear strength (after water immersion) of the PU adhesive glued plywood (PU/plywood) and the SI adhesive glued plywood (SI/plywood) were evaluated. As shown in Table 3, the PU/plywood had a dry shear strength of (2.46 ± 0.20) MPa and a wet shear strength of (0.92 ± 0.06) MPa after water immersion at RT for 24 h, and (0.94 ± 0.04) MPa after hot-water immersion at 63 °C for 3 h. The observed average reduction (above 60%) in shear strength after immersion indicated poor water resistance of the PU adhesive. The dry shear strength of the SI/plywood was (0.92 ± 0.09) MPa, about 63% lower than the value measured for the PU/plywood. However, the performance of the SI adhesive was less sensitive to water immersion at both testing conditions (RT for 24 h and 63 °C for 3 h). For example, the average decrease in wet shear strength (63 °C for 3 h) was about 30% for the SI/plywood and 62% for the PU/plywood. Good water resistance is an expected feature of silicone-based adhesives but, surprisingly, the presence of VSATH in the adhesive increased the wet resistance of SI/plywood. In fact, complete delamination of plywood was observed after water immersion (63 °C for 3 h) when the standard SI formulation containing 65% by mass of VSATH was replaced by a silicone-based adhesive without VSATH (data not shown in Table 3).

3.4. Mydrin test

The Mydrin test was used to assess the effect of the adhesive type on fire-resistance of the plywood samples by comparing the time to burn-through of PU/plywood and SI/plywood. The PU/plywood promptly ignited and the flame spread vertically to the top of the specimen. After about 25 min, the PU/plywood burned through and the ignition flame was removed (Fig. 7). The sample kept burning for additional 5 min and generated a thin char layer along the flame spread path. The SI/plywood did not show burn through even after being exposed to the ignition flame for 60 min. Extinguishment occurred right after removal of the ignition source. The formation of a thin white protective layer over the char, attributed to the formation of silica, was obvious (see Section 3.7). These data indicate a superior fire-resistance performance of the SI/plywood as compared to the PU/plywood.

3.5. Lateral ignition and flame spread test (LIFT)

In the LIFT apparatus, the samples were exposed to a calibrated incident radiant heat flux ($q_{incident}$) that decreased from a maximum value of about 44 kW/m² on the left end of the sample to a minimum value of about 10 kW/m² on the right end of the sample (see Fig. 3). No direct ignition source was used. In this scenario, the PU/plywood auto-ignited about 4 min after the specimen was exposed to the radiant flux. Ignition started from the left side

where the maximum $q''_{incident}$ was reached and flame spread rapidly over the sample. The PU/plywood was removed 5 min after the start of the test. Fig. 8a shows a snapshot during the test and the residue of the PU/plywood after 5 min heat flux exposure. The blue hue in the photo was due to the narrow-spectrum illumination used to enhance visualization of the charring process [50]. At this stage, the PU/plywood surface exhibited extensive charring and delamination. Under the same conditions, no auto-ignition was observed for the SI/plywood after 5 min heat flux exposure (Fig. 8b) and the charred area on the sample surface was noticeably smaller and showed a lower extent of delamination as compared to the PU/plywood. The testing time was increased to 10 min in the subsequent tests. Noticeably, ignition was not observed even after the 10 min exposure time for the SI/plywood and the delamination remained marginal (Fig. 8c). Briefly, the LIFT data results showed a significantly higher ignition and lower delamination tendency of the SI/plywood as compared to the PU/plywood.

3.6. Cone calorimetry and thermocouple measurements

Heat release rate (HRR) is the most important parameter for evaluating reaction-to-fire performance of materials [51,52]. The HRR curves of one representative sample for each plywood type are shown in Fig. 9. For each plywood type, the ignition time (IT), peak heat release rate (PHRR), time to PHRR (TTP), average heat release rate (AHRR), total heat release (THR), and residue are summarized in Table 4.

Fig. 9a shows HRR curves for all the PU adhesive glued plywood samples. The PU/plywood displayed three distinct PHRRs; each of them was associated with the combustion and delamination of a veneer layer in the three-ply sample. After the third PHRR, HRR of the PU/plywood decreased monotonically until flame-out.

Cellulosic (CF) and glass fabric (GF) were added to the composite plywood to enhance the barrier properties of the adhesive system (see PU/CF/plywood and PU/GF/plywood in Table 4 and Fig. 9a). Similar to the PU/plywood, a three-step combustion process was also recorded for these composite samples. The addition of CF or GF to the PU adhesive glued composite plywood marginally decreased the first and second PHRR, but significantly decreased the third PHRR (about 25% reduction for the PU/CF/plywood and 18% reduction for the PU/GF/plywood). The AHRR reductions for the PU/CF/plywood and PU/GF/plywood were about 19% and 26%, respectively, as compared to the PU/plywood. The effect of CF or GF on IT and residue was negligible, *i.e.*, all the PU adhesive glued plywood showed comparable average IT (44 s to 46 s) and residue values (10%–13% by mass).

Fig. 9b shows HRR curves for all the SI adhesive glued plywood samples. The SI/plywood had a significantly superior reaction-to-fire performance than the PU/plywood. The replacement of PU adhesive with SI adhesive in the plywood sample allowed an increase in IT from (44 ± 2) s to (51 ± 1) s, a reduction in the first (most intense) PHRR from (217 ± 15) kW/m² to (160 ± 9) kW/m², an increase in TTP for the third (last) PHRR from (197 ± 15) s to (312 ± 15) s, a reduction in AHRR from (120 ± 5) kW/m² to (76 ± 4) kW/m², a reduction in THR from (38 ± 3) MJ/m² to (31 ± 4) MJ/m², and an increase in residue at the end of the test from (10 ± 3) % by mass to (38 ± 1) % by mass. The addition of CF or GF to the SI adhesive glued composite plywood further improved the reaction-to-fire performance (see

SI/CF/plywood and SI/GF/plywood in Table 4). The average IT values were (51 ± 1) s for the SI/plywood, (58 ± 5) s for the SI/CF/plywood, and (65 ± 8) s for the SI/GF/plywood. The variations in TTP, THR, as well as the first and second PHRR were marginal, but significant reductions of about 33% and 13% in the third PHRR and AHRR, respectively, were observed in the presence of CF or GF.

Thermocouple measurements were conducted simultaneously during cone calorimetry to further characterize the fire-resistance of all the plywood formulations. Triplicate tests were run for each plywood type. The results (average and uncertainties as $\pm$ one standard deviation) are shown in Fig. 10. The temperature for the PU/plywood kept raising throughout the test and reached a maximum of about 700 °C after about 400 s (Fig. 10a). The temperature for the SI/plywood increased until it plateaued at about 600 °C after approximately 400 s (Fig. 10b). The presence of this plateau and a reduction of about 100 °C in the maximum temperature as compared to the PU/plywood indicated the ability of the SI adhesive to generate an effective thermally stable fire barrier.

As expected, the addition of CF or GF improved the barrier effect of the plywood samples. For the PU adhesive glued composite plywood (PU/CF/plywood and PU/GF/plywood in Fig. 10a), it allowed to match the performance of the SI adhesive glued plywood by reducing the maximum temperature from 700 °C to 600 °C. For the SI adhesive glued plywood samples (Fig. 10b), it allowed a temporary reduction in temperature between 100 s and 450 s, but no reduction in the maximum temperature for the SI/CF/plywood, and a reduction in the maximum temperature from about (600 ± 6) °C to about (540 ± 13) °C for the SI/GF/plywood. In summary, the thermocouple measurements indicated that the SI adhesive by itself or the combination of CF or GF with the PU adhesive could generate an effective thermal barrier for the plywood samples, however, the best performance was achieved by combining the SI adhesive with GF.

Fig. 11a shows images for each plywood type captured during cone calorimetry at the time when the 3rd PHRR occurred. All the PU adhesive glued plywood samples delaminated, warped, and broke into fragments during combustion. The SI/plywood showed some delamination, warping, and fragmentation as well. This phenomenon was consistent with previous studies reporting that the combustion residue produced by silicone-based polymers is not self-supporting and can easily fracture and collapse [53]. The addition of CF or GF to the SI adhesive glued composite plywood (see SI/CF/plywood or SI/GF/plywood in Fig. 11a) appeared to suppress delamination and cracking.

Fig. 11 b shows images for each plywood type captured during cone calorimetry at flame-out. All the PU adhesive glued plywood samples showed obvious glowing and smoldering. These samples continued oxidizing after flame-out due to glowing. For example, a carbonaceous residue content of about (21 ± 2) % by mass was measured after flame-out for the PU/plywood (Table 4). Glowing of this residue due to smoldering combustion caused a further decrease to about (10 ± 3) % by mass at the end of the test after additional 300 s (about 52% reduction in residue). As a comparison, no observable glowing and smoldering, and a smaller reduction in residue were observed for all the SI adhesive glued plywood samples. For example, the residue for the SI/plywood decreased from (42 ± 2) % by mass at

flame-out to (38 ± 1) % by mass at the end of the test (about 10% reduction in residue). Fig. 11b also shows that the SI/CF/plywood delaminated after flame-out, while the SI/ GF/ plywood did not. These observations indicated a superior fire performance of the SI/GF/ plywood.

3.7. Analysis of the residue

Images of the residue for each plywood type were captured after completion of cone calorimetry (Fig. 12a). All the PU adhesive glued plywood samples generated a powdery residue with negligible barrier properties. These residues ranged between (10 and 13) % by mass (Table 4). In comparison, residues of the SI adhesive glued plywood samples ranged between (38 and 42) % by mass with a morphology that varied from fragmented (SI/ plywood and SI/CF/plywood) to cohesive without any obvious crack generation (SI/GF/ plywood). The residue from the SI/GF/plywood showed two distinct morphological features: (a) superficial island-like fragments; (b) a cohesive crack-free substrate. The island-like fragments were attributed to the adsorption and accumulation of a thin silica layer over the char produced by the combustion of the top wood veneer layer. The underlying cohesive substrate was attributed to the degradation of the SI adhesive reinforced with GF. The presence of GF in the SI/GF/plywood prevented cracking of the otherwise fragile inorganic residue generated by the SI adhesive. These hypotheses were supported by the SEM imaging and EDS data (see Fig. 12b and c).

SEM imaging and EDS data for an island-like fragment generated by the SI/GF/plywood are shown in Fig. 12b. The residue appeared to be highly porous. The data showed atomic concentrations of (62.70 ± 1.17) atom % for O, (8.35 ± 0.70) atom % for C, and (29.11 ± 1.19) atom % for Si. These values are compatible with the formation of silica and a limited amount of oxidized carbon moieties generated by the degradation of the top veneer layer [54]. For the cohesive underlying substrate (Fig. 12c), SEM imaging showed particles with an average diameter of about 1 μm , and EDS data indicated atomic concentrations of (60.47 ± 0.75) atom % for O, (7.68 ± 0.34) atom % for C, (4.88 ± 0.23) atom % for Si, and (27.17 ± 0.81) atom % for Al. This atomic composition was compatible with a residue generated by the adhesive layer and giving formation to Al_2O_3 (due to the thermal degradation of VSATH [55]), silica (byproduct of the SI adhesive thermal degradation [42]), and thermally stable carbonaceous residues (possibly oxycarbide [54]).

3.8. Mechanisms for flame retardancy in the SI adhesive glued plywood

The SI adhesive glued plywood samples showed a superior fire performance as compared to the PU adhesive glued plywood samples in all the adopted tests (*i.e.*, Mydrin test, LIFT, and cone calorimetry coupled with thermocouple measurements). Both reaction-to-fire (in terms of ignitability and HRR) and fire-resistance (in terms of delamination, time to burn-through and thermal protection) of the SI/plywood was superior to the PU/plywood.

Silicone polymers have an intrinsically lower flammability and higher thermal stability as compared to polyurethanes and their flammability decreases even further when used in combination with a platinum (Pt) catalyst due to enhanced cross-linking [42]. However, the use of several additives (including most fire retardants) is not compatible with Pt-catalyzed

silicone due to Pt poisoning [56], therefore the selection of fire retardants is largely limited. In this work, a halogen-free adhesive based on a silicone elastomer (crosslinked by Pt-catalyzed hydrosilation) and vinylsilane modified aluminum-hydroxide (VSATH) (65% by mass) additive, was adopted. Such an adhesive formulation is expected to have a benign toxicological profile (silicone elastomers are largely used for medical device applications) [57], and to be durable because of the intrinsic properties of the silicone elastomer (excellent chemical, UV, temperature resistance, and adhesion strength) [58] and the use of a surface modification on aluminum hydroxide (ATH) to prevent leaching (see below).

ATH by itself is an effective fire retardant when used at high mass fractions in a material. It decomposes endothermically releasing water and generates an inorganic residue [59]. ATH is particularly effective in Pt-catalyzed silicone when vinyl groups are grafted to the surface of ATH to form VSATH. VSATH is a reactive additive that is capable to crosslink and form covalent bonds with the silicone elastomer during polymerization or thermal degradation. During polymerization, vinyl groups (grafted onto the surface of ATH) take part in to the hydrosilation reaction so that VSATH becomes a part of the crosslinked network. During thermal degradation, unreacted vinyl groups (grafted onto the surface of the inorganic fillers) enhance the residue yield by promoting crosslinking reactions and the formation of a cohesive residue [42]. The thermally stable residue generated by the formulated adhesive acts as an effective mass and heat transfer barrier between wood veneer layers, however, such residue is not self-supporting and can easily fracture and collapse due to its low inherent strength. The addition of a reinforcing phase in the adhesive layer suppressed crack formation. Crack suppression was partial with CF and complete with GF.

Noticeably, the SI adhesive generated a thermally stable residue not only between the plywood layers but also on the surface of the exposed top veneer layer. When exposed to fire, cyclic siloxane (produced by the thermal decomposition of silicone [54]) were transported through the charring veneer layer on the sample surface and subsequently oxidized to form a highly conformal and thermally stable silica layer, thereby suppressing combustion. When an identical silicone formulation was applied to the back side of a cellulosic fabric, both smoldering and flaming of the fabric were prevented by the generation of a conformal silica layer (*i.e.*, a layer that ‘conforms’ to the surface of the substrate) that encapsulated and protected each single fiber [37]. A similar phenomenon was observed here in plywood. The formation of a conformal layer was observed in all the fire scenarios investigated and suppressed glowing (*i.e.*, smoldering combustion) and flaming combustion of the plywood.

4. Conclusions

In this work, a halogen-free flame retardant adhesive for plywood based on a silicone elastomer (crosslinked by Pt-catalyzed hydrosilation) and vinyl-silane modified aluminum-hydroxide (VSATH) (65% by mass) has been compared to a common polyurethane-based (PU) adhesive. The shear strength of such silicone-based (SI) adhesive glued plywood (SI/plywood) [(0.92 ± 0.09) MPa] was about 63% lower than that of the PU adhesive glued plywood (PU/plywood) at room temperature, but it was less sensitive to water (62%

reduction for the PU/plywood and 30% reduction for the SI/plywood after hot-water immersion at 63 °C for 3 h).

The SI/plywood showed a superior fire-resistance (in terms of delamination propensity, time to burn-through and thermal protection) and reaction-to-fire performance (in terms of ignitability and HRR) as compared to the PU/plywood. The PU/plywood burned through after about 25 min in the Mydrin test, and auto-ignited after 4 min with extensive charring and delamination in the LIFT experiment. No ignition was observed for the SI/plywood in either of these two tests, charring and delamination was significantly lower.

Cone calorimetry coupled with thermocouple measurements indicated that the replacement of PU adhesive with SI adhesive in the plywood allowed an increase in time to ignition and thermal protection (about 100 °C reduction in maximum temperature measured on the backside of the sample), and a reduction in heat release rate. In all the SI adhesive glued plywood samples, the characteristic glowing (due to smoldering oxidation of the char) was suppressed by the generation of a conformal silica layer over the charring wood veneer on the exposed surface. At the same time, under the superficial wood veneer, a thermally-stable residue was generated by the decomposition of the formulated SI adhesive. This residue acted as a mass and heat transfer barrier between wood veneer layers, but showed a tendency to fragment and delaminate.

The incorporation of cellulosic fabric (CF) suppressed such fragmentation to a limited extent, whereas glass fabric (GF) fully prevented fragmentation of the residue. As a result, the SI/GF/plywood generated a very effective protective barrier. It showed the best fire performance among all the plywood samples investigated in this study with a 46% reduction in average heat release rate, 24% reduction in total heat release, and reduction in backside maximum temperature of about 150 °C as compared to the PU/plywood.

In conclusion, silicone adhesives may be used in place of the commonly used polyurethane adhesives to improve the fire-resistance and reaction-to-fire performance of plywood without affecting the appearance of the product. The silicone adhesive is expected to be durable and have a benign toxicological profile however further research is required to improve its shear strength. Hybrid adhesive solutions, where the silicone adhesive (possibly in combination with a GF) is used between the two top veneer layers of the plywood and a common polyurethane adhesive is used between the remaining layers, appear to be a promising approach to maximize the benefit-to-cost ratio of such technology. Possible new emerging applications for this technology are cross laminated timber for tall wooden building constructions and exposed laminated wood panels for interior decoration.

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HIGHLIGHTS

- SI adhesive was used to replace conventional PU adhesive to provide a flame-retardant adhesive for plywood.
- SI/plywood showed high flame retardancy and thermal barrier efficiency as compared to PU/plywood.
- SI adhesive was also reinforced with CF or GF to prepare composite plywood with improved fire performance.
- SI/GF/plywood exhibited the most effective fire barrier among all plywood types.

Fig. 1.
Preparation of the plywood samples: (a) plywood without CF/GF; (b) plywood with CF/GF.

Fig. 2.
Mydrin test rig.

Fig. 3. Schematic drawing showing the LIFT setup (*i.e.*, dimensions and position of the sample and frame) and the incident radiant heat flux profile.

Fig. 4. Thermocouples coupled with the cone calorimetry samples (not to scale).

Fig. 5.
FTIR spectra of the adhesives.

Fig. 6.
Representative (a) TGA and (b) DTG curves of the adhesives.

Fig. 7.
Images captured at different times during the Mydrin tests and after flame-out for the PU/
plywood and the SI/plywood.

Fig. 8.
Images of the samples during LIFT experiments and the sample residues. (a) PU/plywood tested for 5 min; (b) SI/plywood tested for 5 min; (c) SI/plywood tested for 10 min.

Fig. 9.
HRR curves of one representative for (a) the PU adhesive glued plywood samples and (b) the SI adhesive glued plywood samples.

Fig. 10. Dynamic temperatures measured for (a) the PU adhesive glued plywood samples and (b) the SI adhesive glued plywood samples.

Fig. 11.

Images of one representative sample for each plywood type captured during cone calorimetry at (a) the time when the 3rd PHRR occurred and (b) flame-out.

Fig. 12.

- (a) Images of one representative residue for each plywood type after cone calorimetry test;
 (b) SEM imaging and EDS data for a superficial island-like residue generated by the SI/GF/plywood; (c) SEM imaging and EDS data for the cohesive substrate produced by the SI/GF/plywood (Uncertainties shown as $\pm$ one standard deviation).

Table 1

Compositions for the PU adhesive glued plywood samples (PU/plywood, PU/CF/plywood, and PU/GF/plywood) and the SI adhesive glued plywood samples (SI/plywood, SI/CF/plywood, and SI/GF/plywood), including wood, adhesive (PU or SI), fabric (CF or GF) content and adhesive-to-wood mass ratio (uncertainties shown as $\pm$ one standard deviation).

Plywood type	Wood (g)	PU/SI (g)	CF/GF (g)	Adhesive-to-wood mass ratio (%)	
				Before hot pressing	After hot pressing
PU/plywood	26.3 $\pm$ 0.4	5.2 $\pm$ 0.3	-	20 $\pm$ 1	15 $\pm$ 1
PU/CF/plywood	26.8 $\pm$ 0.3	5.4 $\pm$ 0.1	2.223 $\pm$ 0.037	20 $\pm$ 1	16 $\pm$ 1
PU/GF/plywood	26.7 $\pm$ 0.5	5.3 $\pm$ 0.2	0.382 $\pm$ 0.005	20 $\pm$ 1	15 $\pm$ 1
SI/plywood	26.3 $\pm$ 0.5	15.8 $\pm$ 0.4	-	60 $\pm$ 1	51 $\pm$ 2
SI/CF/plywood	26.2 $\pm$ 0.5	15.7 $\pm$ 0.3	2.234 $\pm$ 0.017	60 $\pm$ 1	52 $\pm$ 1
SI/GF/plywood	26.6 $\pm$ 0.4	16.0 $\pm$ 0.2	0.383 $\pm$ 0.004	60 $\pm$ 1	50 $\pm$ 2

Table 2

TGA data of the adhesives (uncertainties shown as $\pm$ one standard deviation).

Samples	T_{max1} ($^{\circ}$ C)	MLR_{max1} b ($\%/^{\circ}$ C)	T_{max2} c ($^{\circ}$ C)	MLR_{max2} d ($\%/^{\circ}$ C)	Residue at 800 $^{\circ}$ C (% by mass)
PU	325 ± 1	1.42 ± 0.03	451 ± 1	0.31 ± 0.01	5 ± 2
SI	285 ± 2	0.35 ± 0.03	458 ± 1	0.15 ± 0.01	60 ± 1

a Temperature at which the first DTG peak occurred.

b Mass loss rate value measured at the first DTG peak.

c Temperature at which the second DTG peak occurred.

d Mass loss rate value measured at the second DTG peak.

Table 3

Shear strength of the plywood samples (uncertainties shown as $\pm$ one standard deviation).

Plywood type	Shear strength (MPa)		
	Dry	Wet (RT, 24 h)	Wet(63°C, 3 h)
PU/plywood	2.46 ± 0.20	0.92 ± 0.06	0.94 ± 0.04
SI/plywood	0.92 ± 0.09	0.54 ± 0.03	0.64 ± 0.03

Table 4

Cone calorimetry data of the plywood samples (uncertainties shown as $\pm$ one standard deviation).

Plywood type	IT (s)	PHRR (kW/m ²)			TTP ^a (s)			AHRR (kW/m ²)	THR (MJ/m ²)	Residue (% by mass)	
		1st	2nd	3rd	1st	2nd	3rd			Flame-out ^b	Final ^c
PU/plywood	44 $\pm$ 2	217 $\pm$ 15	169 $\pm$ 11	193 $\pm$ 18	75 $\pm$ 12	143 $\pm$ 12	197 $\pm$ 15	120 $\pm$ 5	38 $\pm$ 3	21 $\pm$ 2	10 $\pm$ 3
PU/CF/plywood	46 $\pm$ 2	178 $\pm$ 3	163 $\pm$ 5	144 $\pm$ 7	71 $\pm$ 4	168 $\pm$ 6	230 $\pm$ 13	97 $\pm$ 6	39 $\pm$ 4	22 $\pm$ 1	12 $\pm$ 3
PU/GF/plywood	46 $\pm$ 2	190 $\pm$ 7	160 $\pm$ 2	159 $\pm$ 2	68 $\pm$ 2	157 $\pm$ 13	226 $\pm$ 15	89 $\pm$ 9	38 $\pm$ 3	25 $\pm$ 1	13 $\pm$ 2
SI/plywood	51 $\pm$ 1	160 $\pm$ 9	156 $\pm$ 11	135 $\pm$ 14	76 $\pm$ 15	188 $\pm$ 14	312 $\pm$ 15	76 $\pm$ 4	31 $\pm$ 4	42 $\pm$ 2	38 $\pm$ 1
SI/CF/plywood	58 $\pm$ 5	146 $\pm$ 11	157 $\pm$ 9	91 $\pm$ 4	75 $\pm$ 2	197 $\pm$ 4	322 $\pm$ 8	66 $\pm$ 3	34 $\pm$ 1	41 $\pm$ 1	39 $\pm$ 2
SI/GF/plywood	65 $\pm$ 8	151 $\pm$ 3	140 $\pm$ 17	91 $\pm$ 10	76 $\pm$ 5	194 $\pm$ 15	313 $\pm$ 6	65 $\pm$ 7	29 $\pm$ 1	45 $\pm$ 1	42 $\pm$ 1

^aTime to PHRR.

^bResidue mass fraction % at flame-out.

^cResidue mass fraction % at the end of the cone calorimetry test (300 s after flame-out).