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# Evaluation of Irvingia kernels extract as biobased wood adhesive

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## Abstract

Irvingia tree species have been earmarked for domestication in many countries due to their potential as raw materials for various applications, which include biodiesel, cosmetics, perfume, soap, etc. Presently, there is no information on the utilization of kernel seed extract as a potential source of green wood adhesive. This study is focused on investigating the properties of adhesives produced from kernel seeds of two Irvingia wood species i.e. *Irvingia gabonensis* (IG) and *Irvingia wombolu* (IW), as well as investigating the improved properties derived from the effect of modification using a few selected modifying agents including glutaraldehyde, glyoxal, epichlorohydrin (EPI) and an acid/base type process modification. Polyethylene (PE) was used along with the glutaraldehyde, glyoxal and epichlorohydrin modifiers in the modification process. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were conducted to study the effect of modification on adhesive properties. The glycosidic carbon of the unmodified extracts and that of the EPI modified sample were not sensitive to chain conformations. Principal components (PC) 1 and 2 explained 85.19 and 9.54%, respectively, of the total variability in FTIR spectra among the modified and unmodified adhesives. The unmodified samples for IG and IW exhibited one peak with crystallization temperatures of 18.7 and 14.4 °C, respectively, indicating only one component exhibits some low degree crystallinity. The adhesive properties of the modified extracts were tested on wood veneers according to ASTM standard. The shear strength of the modified adhesives ranged from 1.5 to 3.93 MPa and 1.7 to 4.05 MPa for IG and IW, respectively. The modified samples containing PE showed marked improvement in the shear strength. The highest values were about 63% higher than the shear strength of unmodified samples with least shear strength. The results indicated that the modification of Irvingia-based adhesives had a great contribution to their performance as natural wood adhesives.

**Keywords:** *Irvingia gabonensis*, Irvingia kernel extracts, *Irvingia wombolu*, Natural wood adhesive, Wood adhesive modification, Wood composites

## Introduction

It is well established that the global demand for wood composites has increased tremendously over the last two decades [1]. With increasing awareness of the impact of the hazardous levels of volatile organic compounds' emission, especially formaldehyde from wood composite products bonded with formaldehyde-based adhesives, it is becoming imperative to find viable alternatives, which are less

harmful to humans and the environment [2]. The role of adhesives cannot be overemphasized for the efficient utilization of wood and other lignocellulosic resources in the manufacturing of wood products [3]. Products from wood composite industries such as particleboard, oriented strand board, plywood and laminated timber are essential, and they are being used for the production of wooden trusses, kitchen cabinets, wardrobes, bookshelves, etc. Formaldehyde-based adhesives, which include urea formaldehyde, phenol formaldehyde, melamine formaldehyde and resorcinol are the most commonly used adhesives because of their excellent performance, which includes good adhesion

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to different lignocellulosic substrates, high water resistance (except for urea formaldehyde), low initial viscosity, resistance to environmental degradation, and excellent thermal stability [4]. These formaldehyde-based adhesives are produced from petroleum and natural gas which are non-renewable resources [5]. Furthermore, the emission of hazardous compounds from composite products manufactured with these adhesives is of great concern because of their effect on health-related issues. As a consequence, they were categorised among the carcinogenic materials by the World Health Organisation (WHO) in 2004 [5]. Therefore, recent studies have focused on the development of wood adhesives from renewable sources, which are environmentally safe and able to compete with conventional adhesives with regards to performance properties [6].

Irvingia species belong to the family Irvingiaceae. The species include *I. gabonensis* (IG), *I. wombolu* (IW), *I. smithii* (IS), *I. grandiflora* (IGF), *I. robur* (IR) and *I. malayana* (IM). *I. malayana* is usually found in South-east Asia [7]. IG and IW are the most commonly found in Africa. These two species are very similar and difficult to distinguish. The distinction between the two species is that IG has sweet edible fruit pulp, while IW has bitter, inedible fruit pulp. In West Africa, they are commonly known as Dika nut, bush mango or wild mango. Irvingia prefers undisturbed low land tropical forest as their habitat and the species is well adapted to Ultisol soils in high rainfall areas. These forest fruit trees are widely available in western and central African countries. They are now being domesticated in many countries because of their numerous potential uses [8]. Irvingia trees usually reach maturity and begin flowering at 10–15 years of age. However, much earlier fruiting has been reported. Ladipo [9] described trees that produced fruit at age six.

Several studies have shown that various products, such as fuel (bio-diesel), cooking oil, cosmetics, margarine, season cubes, confectionaries and soaps, can be produced from the oil (fat content) from Irvingia kernels [10, 11]. However, limited information is available on the potential application of the residues (mucilage). Some researchers have used mucilage to formulate drug binders in medical formulations. This mucilage is starch based. There was also an attempt by Ikechukwu and Salome [12] to evaluate the possibility of using gum from IW kernels in the tramadol capsule production. The authors concluded that the gum has good potential to be used in producing normal tramadol capsules. Recently, Alawode et al. [13] reported that adhesives extracted from kernels of IG and IW have the potential to be used as wood adhesives. However, the adhesive properties could be improved by cross linking with other substrates [13]. Currently, there is no information on the properties and characterization of modified Irvingia adhesive using different modifiers.

Many studies have been carried out on the modification of numerous potential wood adhesives developed from different natural sources such as tannins, lignin, citric acid, carbohydrate, unsaturated oils, liquefied wood, rice bran, and soybean proteins [5, 14–17]. Imam et al. [18] successfully developed wood adhesive by blending starch polymers with polyvinyl alcohol (PVOH), hexamine, citric acid and latex. In another report, oxidized starch adhesives were modified to improve their performance by incorporating sodium dodecyl sulfate, urea, silane couplings and olefins. The authors reported that bonding strength and water resistance of the adhesive were significantly improved [19]. Umemura et al. [20] investigated the properties of boards manufactured from citric acid and sucrose adhesive, and reported excellent physical properties. Particleboards have also been manufactured from sweet sorghum bagasse and citric acid adhesive [21].

Polyethylene (PE) is well known for its high mechanical and impact strength and is widely used in day-to-day life applications such as insulation cable and construction materials. PE has chemically inert surfaces with low surface energy. This makes them difficult to bond with other substrates. These materials are highly chemically robust and exhibit very poor adhesive properties on their own. In this study, we provided information on the modification of IG and IW kernel extract as an adhesive from a renewable source (wood) using different hardeners as crosslinking agents as well as blending these modified extracts with PE to produce wood adhesives of greater mechanical strength. For the first time, the effective use of modified kernel seed extracts/PE blend as potential wood binder was demonstrated. The extract was modified chemically with some selected hardeners, which was followed by blending of the modified extract with PE. The chemical and thermal properties of the product were analysed using fourier transform infrared spectroscopy (FTIR), solid-state nuclear magnetic resonance (NMR), thermogravimetric analyser (TGA) and differential scanning calorimetry (DSC). The effect of glyoxal/PE, epichlorohydrin/PE, glutaraldehyde/PE, acid/base modification on composition and functional groups of Irvingia wood adhesives was also investigated.

## Materials and methods

IG and IW kernels were purchased from a local market in Nigeria. Sigma Aldrich, Co., USA supplied epichlorohydrin 99%, Glyoxal solution (40 wt% in water), Glutaraldehyde solution (Grade II, 25% in water), Hexamethoxymethylmelamine (Hexamine), Hydrochloric acid (HCl 37%), and Dicyandiamide (99%). The sodium hydroxide (NaOH 97%) used was supplied by Science World, South Africa. Ferric Chloride Hexahydrate (99–102%) was purchased from Merck (Pty) Ltd, South Africa. Bondtite 345 was supplied by Bondtite® Pty Ltd, South Africa.

**Adhesive extraction**

The extraction of adhesives from both species of kernels was carried out according to the method employed by Eraga et al. [22] with slight modification. According to the method, 100 g of the powdered cotyledon of IG and IW were dispersed in 2 L of distilled water in a plastic container. The mixture was gently stirred for 1 h with the aid of magnetic stirrer. The dispersion was homogenized for about 1 h using PRO250 homogenizer, and left for 24 h. The mucilage formed was then filtered through a clean muslin cloth to obtain a viscous filtrate (gum). The gum was centrifuged (Allegra 6R centrifuge, Beckman Coulter™, USA) at 3440 rpm for 10 min to separate the fat. The gum was thereafter freeze-dried for further use.

**Compositional analysis**

The kernels of both species were air-dried for 14 days. Thereafter, they were milled using a hammer mill fitted with a 1 mm sieving slice. The obtained ground cotyledon and the kernel extract were analysed for protein, fat, ash and carbohydrate contents using the Association of Official Analytical Chemists Methods [23]. This method was used because it is the most comprehensive collection of chemical and microbiological methods available.

**Adhesives modification**

The modification procedure was adapted from Imam et al. [17] and Sulaiman et al. [21]. Modification of the adhesives

was carried out using different hardeners, namely epichlorohydrin, glutaraldehyde and glyoxal to establish which hardener resulted in the best performance properties (see Table 2). 50 g of modified adhesive was prepared by dissolving the freeze-dried extract (14.7 g) in distilled water (27.5 mL). The mixture was stirred at 60 °C for 1 h using a magnetic hotplate/stirrer. The solution was cooled to 25 °C. 4.8 mL of each hardener and 3 g of PE were added separately to the solution to produce the binder. Volumes were adjusted for loss of water. Each mixture was continuously stirred for 10 min, and then left to cool to room temperature. The acid/base modification was done according to the method employed by Chen et al. [25]. This method involved modification with hydrochloric acid, salt, dicyandiamide and alkali. According to this method, 200 mL of distilled water was added to 5 g of extract in a beaker. The mixture was stirred at a speed of 100 rpm at 35 °C for 60 min. Then, 0.6 M hydrochloric acid (37%) solution was added and stirred at 120 rpm for 30 min. Thereafter, 0.2 g of dicyandiamide (99%) was added and stirred for another 60 min. Finally, 2 g of sodium hydroxide (97%) pellet was added to the above mixture and stirred for 10 min. The modified samples were freeze-dried for about 23 h, milled into powder and kept in sealed plastic bags for further characterization and tests. For convenience, the names of the extracts, the modifier and notation of all the samples are presented in Table 1. Table 2 presents the formulation parameters for the Irvingia-based adhesives.

**Table 1 Extract origins, modification methods and abbreviations of the samples**

Extract name	Modifier	Notation	Extract name	Modifier	Notation
<i>Irvingia gabonensis</i> (IG)	Unmodified	IGN	<i>Irvingia wombolu</i> (IW)	Unmodified	IWN
	HCl/NaOH	IGC		HCl/NaOH Epichlorohydrin	IWC
	Epichlorohydrin	IGE		Glutaraldehyde	IWE
	Glutaraldehyde	IGG		Glyoxal	IWG
	Glyoxal	IGLY			IWLY

**Table 2 Formulation parameters for unmodified and modified Irvingia-based adhesives**

Samples	Extract (g)	Hardeners	Water (mL)	Polyethylene (g)
IGN	14.7	No hardener	27.5	No polyethylene
IGC	5	HCl, NaOH and dicyandiamide	200	No polyethylene
IGE	14.7	Epichlorohydrin	27.5	3
IGG	14.7	Glutaraldehyde	27.5	3
IGLY	14.7	Glyoxal	27.5	3
IWN	14.7	No hardener	27.5	No polyethylene
IWC	5	HCl, NaOH and dicyandiamide	200	No polyethylene
IWE	14.7	Epichlorohydrin	27.5	3
IWG	14.7	Glutaraldehyde	27.5	3
IWLY	14.7	Glyoxal	27.5	3

### Nuclear magnetic resonance (NMR) spectroscopy

The modification of Irvingia-based adhesives was verified with solid-state  $^{13}\text{C}$  NMR using a Bruker Avance III 400 MHz equipment (Billerica, MA, USA). This was carried out to observe the structural changes in the adhesives after modification process. The spectra were recorded using a decoupled sequence at  $^{13}\text{C}$  frequency of 100.6338 MHz at 25 °C. Samples were measured at a spinning rate of 10,000 Hz averaging 4096 scans with a recycling delay of 10 s. A time domain of 2 K was employed with a spectral width of 30 kHz.

### Fourier transform Infrared (FTIR) spectroscopy

The modified and unmodified adhesive samples were analysed with FTIR spectroscopy operated in attenuated total reflectance (ATR) mode. This analysis was done to further monitor changes in the structures of Irvingia adhesives upon modification. The freeze-dried powdered samples of about 2.4% moisture content were pressed against the diamond crystal surface with a spring-loaded anvil of a Thermo Nicolet, Nexus™ model 470/670/870 FT-IR spectrometer equipped with ZnSe lenses. Spectra were collected in ATR mode at a resolution of  $4\text{ cm}^{-1}$  and 32 scans per sample within the absorption bands in the region of 4000–650  $\text{cm}^{-1}$ . Data collection and further processing were carried out in the Thermo Scientific OMNIC software as described by Naron et al. [26]. Principal component analysis (PCA) was performed using Statistica (Statsoft V12) to distinguish between the spectra pattern exhibited by the different modified adhesive samples.

### Differential scanning calorimetry (DSC)

DSC analysis was carried out according to the method employed by Ahire et al. [27]. This analysis was performed to observe the thermal behaviour as the samples were subjected to a temperature profile. The melting and crystallization temperatures of the endothermic and exothermic phases, respectively, were determined using a TA Instruments Q100 calorimeter. The instrument was calibrated with an indium metal standard according to standard procedures. About 4 mg of the powdered samples were placed into an aluminium pan. The samples were then transferred to the heating pan, with the usage of empty pan as reference. The samples were heated and cooled at a rate of 10 °C/min in the temperature range of –15 and 150 °C under inert nitrogen atmosphere.

### Thermogravimetric analysis (TGA)

TGA was performed to evaluate the thermal stability of the adhesive. The analysis of the samples was done using

a TGA Q50 thermogravimetric apparatus. About 5 mg of each powdered sample was placed on a balance located in the furnace and heat was applied over the temperature range from room temperature to 600 °C at a heating rate of 20 °C/min in a nitrogen atmosphere. The derivatives of weight loss vs temperature thermograms were obtained to show the different decomposition processes.

### Scanning electron microscopy (SEM)

SEM analysis of unmodified and modified adhesives was conducted to study the effect of modifications on the morphological features of the adhesives. The freeze-dried powder samples were mounted on aluminium stubs using double-sided conductive carbon tape, and conductivity was enhanced using carbon evaporation (Quorum Technologies Q150T ES). The micrographs of the unmodified and modified samples were examined using a Zeiss Merlin FE-SEM (Carl Zeiss Microscopy, Germany) operated at 5 kV and 200 pA beam current, using inLens secondary electron (SE) and SE2 detection. The SEM was equipped with an energy dispersive X-ray spectrometer (EDS). EDS elemental analysis was done at 20 kV using a Zeiss EVO MA15 SEM and Oxford Instruments X-Max 20  $\text{mm}^2$  detector with Oxford INCA software (Oxford Instruments, Oxfordshire, UK).

### Shear strength test

The shear strength properties of the modified adhesives were determined according to ASTM D 906-64 test method [28]. This test method covers the determination of the comparative shear strengths of adhesives in plywood-type construction, when tested on a standard specimen and under specified conditions of preparation, conditioning, and testing. This test was carried out by tension loading using the Instron Universal testing machine. Three-layer plywood of 9 mm was prepared from sweet birch (*Betula lenta*) veneer with a thickness of 3 mm. Each veneer was coated with 250  $\text{g/m}^2$  of adhesive and exposed to air for about 15 min to evaporate excessive moisture. This procedure was repeated with a commercial tannin-based resin, Bondtite 345 for comparison. Glued veneers were hot-pressed at 150 °C with an applied pressure of 1.6 MPa for 10 min. Ten replicates of each sample were prepared. The test specimens were placed in a conditioning room at 65% relative humidity (RH) and 20 °C for 96 h prior to the strength test. The test specimen was placed in the jaws of the grips in the testing machine so that it aligned perfectly and parallel to the centerline of the jaws. The load was applied at a rate of 700 lb/min until failure. The shear strength was calculated as the failing load per shear area.

## Results and discussion

### Chemical composition of kernels

For a detailed compositional assessment of the kernels, a proximate analysis was carried out on the ground cotyledon and extracts of IW and IG. The samples were subjected to carbohydrate, protein and fat tests to determine their contents according to AOAC methods [23]. The chemical composition of the samples are presented in Table 3. The results are in agreement with those reported by Ikhatua et al. [29], although a small variation in the proportion of constituents was observed. These differences might be due to differences in the source of the seeds. The compositional analysis of the crude samples illustrated that fat constitutes the major component. Upon extraction in water, the samples were defatted and analysed (Table 3). In the case of IW, approximately 2% of the protein content was lost after water extraction, while the other components increased proportionally.

To observe the structural changes due to modifications, all the adhesive samples were characterized using

solid-state  $^{13}\text{C}$  NMR, FTIR spectroscopy, DSC, SEM, EDS and TGA. The results of the different analysis are described as follows;

### Solid state $^{13}\text{C}$ NMR analysis

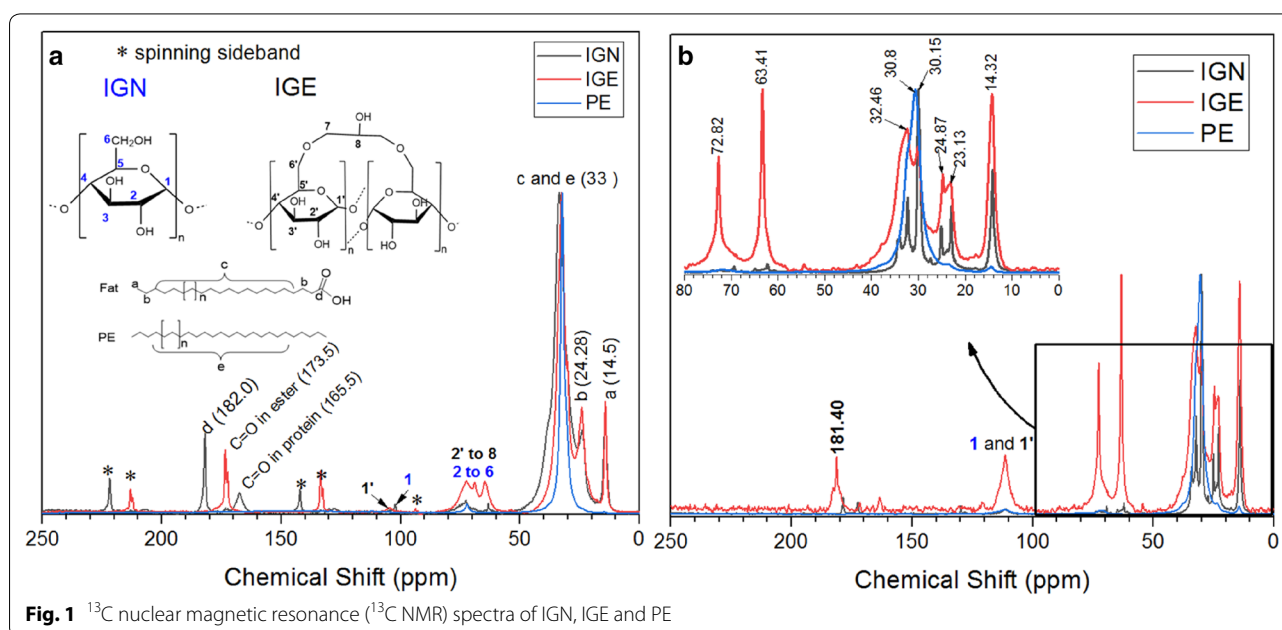
The chemical structure analysis of the samples was first performed using solid-state  $^{13}\text{C}$  NMR as depicted in Fig. 1. The molecular structure of epychlorohydrine modified *I. gabonensis* (IGE) was compared to that of unmodified *I. gabonensis* (IGN) and PE to observe possible structural changes that may have occurred after modification. The glycosidic carbon of IGN designated **1**, and that of the EPI modified sample designated **1'** are not sensitive to chain conformations; therefore, resonate as a very weak peak at 110 ppm [19].

The peaks resonating at 183 and 165 ppm correspond to the carbonyl carbon assigned **d** of the fatty acid and that of the amide moiety of the protein component (not shown), respectively [19, 30]. The resonating peak at 23.1 and 14.3 are due to methyl and

**Table 3** Chemical composition of IW and IG kernels content before and after defatting in water

Species	Extraction method	Carbohydrate (%)	Protein (%)	Fat (%)	Ash (%)	Moisture content (%)
IW	Crude	21.2 (0.82)	6.5 (0.36)	67.5 (1.69)	2.3 (0.05)	2.5 (0.05)
IG	Crude	16.83 (0.82)	7.97 (0.51)	70.5 (1.92)	2.4 (0.08)	2.3 (0.08)
IW	Water	43.5 (0.16)	4.77 (0.28)	40.2 (5.6)	6.1 (0.12)	5.4 (0.25)
IG	Water	39.8 (0.31)	7.92 (0.76)	41.5 (0.7)	6.6 (0.16)	4.1 (0.25)

Values represent mean of three replicates with standard deviation in parenthesis





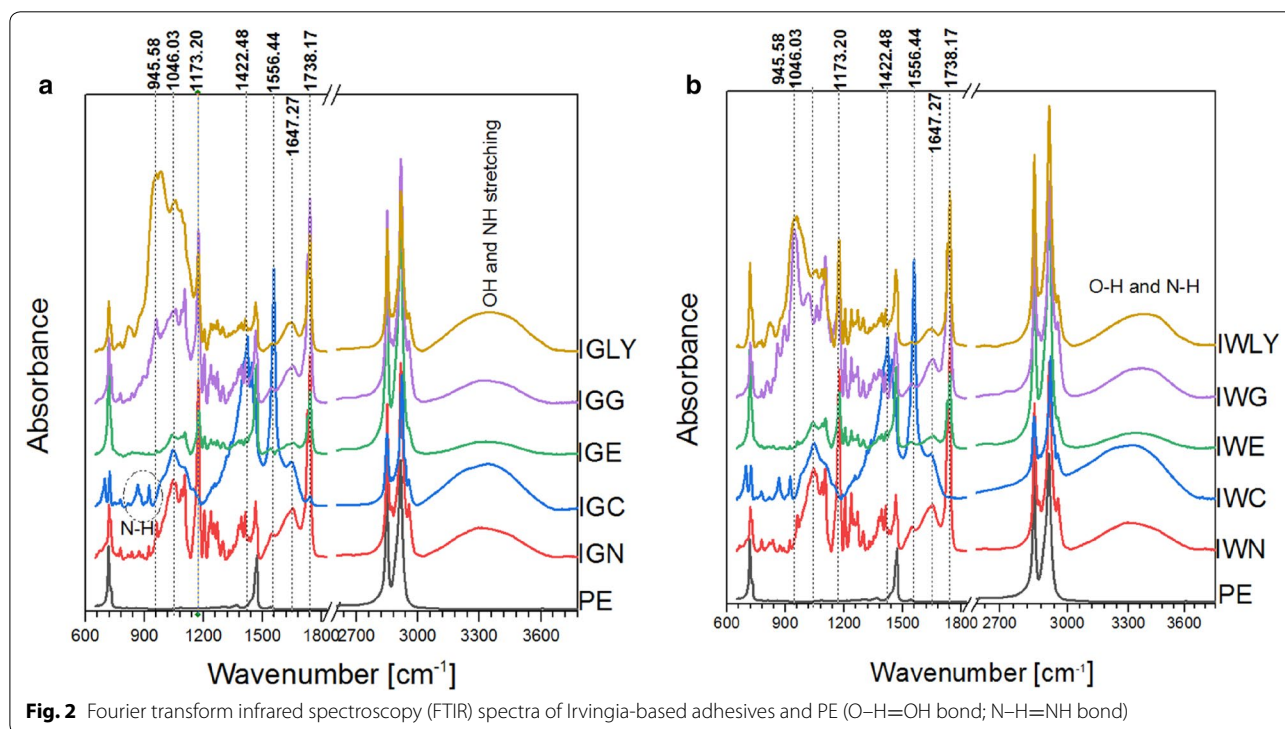
methylene carbons assigned as **a** and **b** of the fatty acid moiety, while the backbone carbons assigned as **2** to **5** of the starch ring and the methylene carbon **c** of the fatty acid backbone resonate as a broad peak at 33 ppm. These peaks are observed as multiplet between 32 and 30 ppm as seen on the carbon depolarised (DP) plot presented in Fig. 1b. The plot representing the epichlorohydrin/PE modified samples, illustrates chemical shift change of the carbonyl carbon associated with the carboxylic acid functionality, and is observed to resonate at 173 ppm. This indicates changes in the chemical environment in IGE. This change may be due to the esterification reaction between epichlorohydrin and fatty acid. In addition, the emergence of new peaks between 80 and 60 ppm is due to carbon labelled **6**, **6'**, **7** and **8** of the epichlorohydrin linkage, which is also associated to the two peaks resonating at 72 and 63 ppm in Fig. 1b. In addition, methylene carbons of the PE and ester backbone are seen to merge at 33 ppm, which are observed at 30.8 ppm in the DP plots (Fig. 2) [31].

#### FTIR analysis

As a complementary technique, FTIR was used to assess any change in the molecular structure of the adhesive samples after modifications. The spectra of IGN and unmodified *I. wombolu* (IWN) were compared to the modified extracts as seen on the stack plot in Fig. 2.

The broad band between 900 and 1200  $\text{cm}^{-1}$  is associated with polysaccharides moiety, while the peak at 1173  $\text{cm}^{-1}$  is due to C=O vibration of the glycosidic linkage (C–O–C) [32]. The band at 1046  $\text{cm}^{-1}$  is assigned to the C–N stretching of the amide linkage of the protein backbone [33]. The peaks at 1556 and 1647  $\text{cm}^{-1}$  are attributed to the amide I (C=O stretching) and amide II (NH bending) vibrations of the protein component [34]. The  $\text{CH}_2$  rocking and bending vibrations of the fatty acid backbone are observed at 714, 1471  $\text{cm}^{-1}$ , while the symmetrical and asymmetrical stretching are seen at 2916 and 2846  $\text{cm}^{-1}$ , respectively. The sharp peak observed at 1738  $\text{cm}^{-1}$  is ascribed to the carbonyl stretching vibration of the carboxylic acid functionality of the fatty acid [35]. The broad band at 3300  $\text{cm}^{-1}$  may be due to OH bond stretching of the starch and fat, as well as NH stretching of the amino group pertaining to the protein component. Qualitatively, these results correlate well with the observations reported in Table 2.

Different from the unmodified extracts, hydrolysis of the starch and protein components with hydrochloric acid is reported in acid/base modified *I. gabonensis* and *I. wombolu* (IGC and IWC). It is well documented that the acidification of starch and protein under appropriate conditions may result in depolymerisation of the respective sugar and amino acid moieties [36]. In the case of the HCl/NaOH hydrolysed samples IGC and IWC, the disappearance of the C=O vibration band at 1173  $\text{cm}^{-1}$



indicates the cleavage of the glycosidic linkage (C–O–C) of the starch component [32]. In addition, the complete disappearance of the carbonyl stretching vibration at  $1737\text{ cm}^{-1}$  indicates complete hydrolysis of the fatty acid by NaOH to form sodium carboxylate, which resulted to a complete resonance between the carbonyl bond end of the acid and carboxylate group. It was reported that carboxylate do not show carbonyl stretching but rather strong vibration at  $1422$  and  $1556\text{ cm}^{-1}$ , which are associated to the asymmetrical and symmetrical vibration of the C=O bond of the carboxylate group [35]. Identical observations were observed for IWC as shown in Fig. 2b. No major structural changes could be associated with the modified samples with glyceraldehyde and glyoxal except for the polysaccharides band between  $900$  and  $1200\text{ cm}^{-1}$ . In this region, stranger vibration bands are seen for glyoxal modified *I. gabonensis* and *I. wombolu* (IGLY and IWLY) when compared to the other modified samples; while IGE and epychlorohydrin modified *I. wombolu* (IWE) show the lowest, admitting structural changes amongst the different samples (Fig. 2).

### Principal component analysis (PCA)

PCA was used to determine the differences within the fingerprint regions of the FTIR spectra among the adhesives (Fig. 3). A PCA is a multivariate ordination analysis, which orders samples in a plane typically defined by two axes (PC1 and PC2) according to their continuous variables. According to the PCA score plot (Fig. 3), PC1 and PC2 explained 85.19 and 9.54%, respectively, of the total variability in FTIR spectra among the modified and unmodified adhesives. The projection on the PCA results on PC1 and PC2 identified three different clusters based

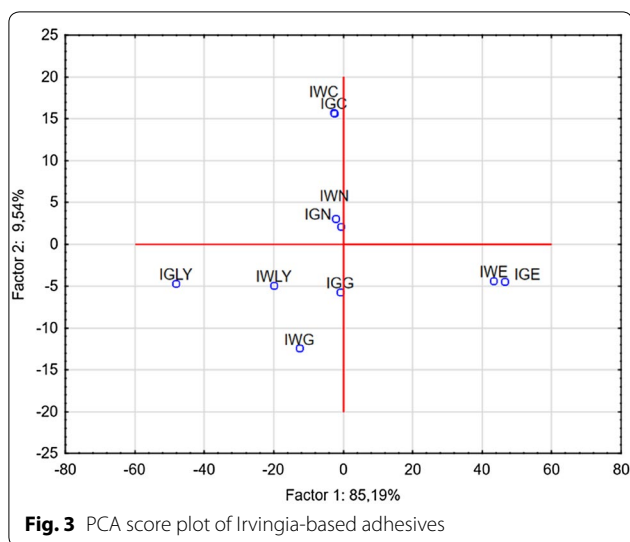
on species and modifiers. PC1 separated epichlorohydrin modified samples (positive loadings) from the other samples. The adhesives modified with epichlorohydrin (IGE and IWE) were isolated from other adhesives at the positive side of PC1, very close to the centerline.

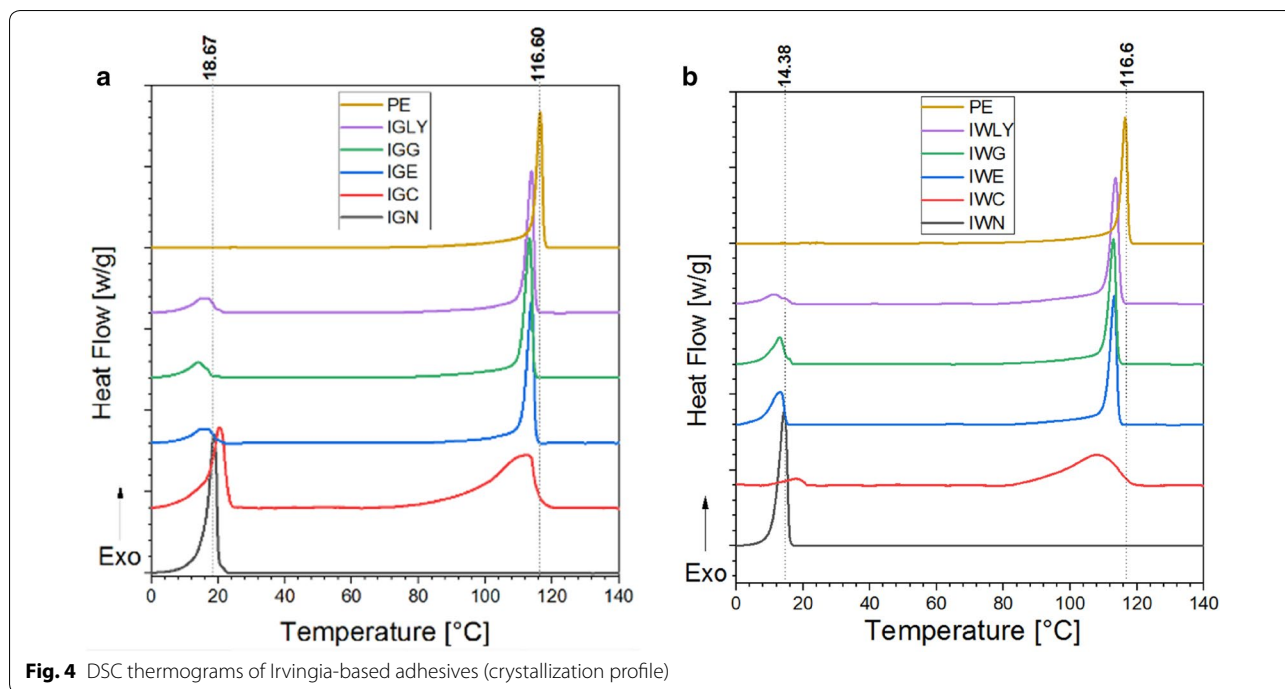
This may be due to the absence of the absorption band at  $1728\text{ cm}^{-1}$ , which is attributed to the C=O stretching vibration of carboxyl groups. The adhesives modified via acid/base modification process (IWC and IGC) are located at the top negative side of the PC1. This could be partly due to the presence of carbonyl ester, located at  $1740\text{ cm}^{-1}$  in these adhesives. On PC2, The adhesives modified with acid/base modification process and unmodified adhesives are located on positive side of PC2, very close to the centerline. Glyoxal, epichlorohydrin and glutaraldehyde modified samples are located on the negative side of PC2. This may be due to the presence of a peak at  $1379\text{ cm}^{-1}$ , which corresponds to symmetric COO stretching.

### DSC analysis

The unmodified and modified samples were analysed with DSC to observe their thermal behaviour as the samples were subjected to a temperature profile. The thermograms presented in Fig. 4a, b illustrate the crystallization profiles as recorded during the first cooling cycle. As can be seen, the unmodified samples (IGN and IWN) exhibit one peak with crystallization temperatures of  $18.7$  and  $14.4\text{ }^{\circ}\text{C}$ , respectively, meaning only one component amongst the many present exhibits some degree of being crystalline with very low crystallinity. This melting temperature can be associated to longer fatty acid backbone. On the other hand, the peak around  $116.6\text{ }^{\circ}\text{C}$  represents the crystallization temperature of the polyethylene backbone that was used during modification.

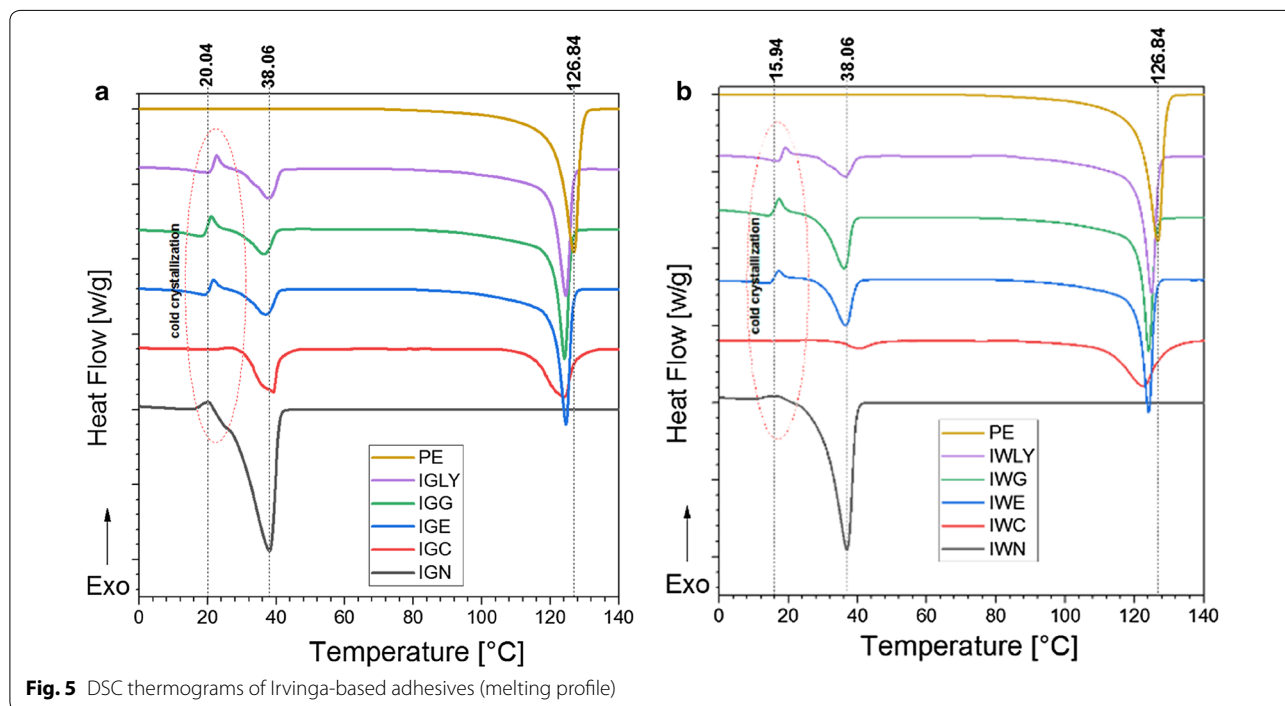
After modification, IGE, IGG and IGLY display two peak crystallization temperatures at  $15$  and  $113\text{ }^{\circ}\text{C}$ . These peaks are attributed to the extract and PE moieties, respectively, and are typical of a blend. When comparing the peak, which is associated with the modified extract (at  $15\text{ }^{\circ}\text{C}$ ) to that of the unmodified samples, a shift toward lower crystallization temperature is observed as indicated by the dotted line, and is attributed to changes in the chemical structures. In the case of IGC, a slight shift toward higher peak crystallization temperatures is seen. It should be noted that this sample contains no PE. Therefore, the broad crystallization peak around  $112\text{ }^{\circ}\text{C}$  is associated with sugar that resulted from the depolymerization of the starch (cleavage of the glycosidic linkage) [37]. Similar observations were seen with IWN and the modified samples although lower peak temperatures are reported.





The melt endotherms of the associated samples are shown in Fig. 5a, b and were recorded from the second heating cycle. The first heating was used to erase the thermal history. The unmodified samples IGN undergoes cold crystallization at 20 °C, and subsequent melting at

38 °C. This behaviour is typical of adhesive polymers [38] and such low melting temperatures are associated to fatty acid with longer CH<sub>2</sub> backbone as was earlier reported by Knothe and Dunn [39]. On the other hand, the PE used in the modification is observed at 126.8 °C. After







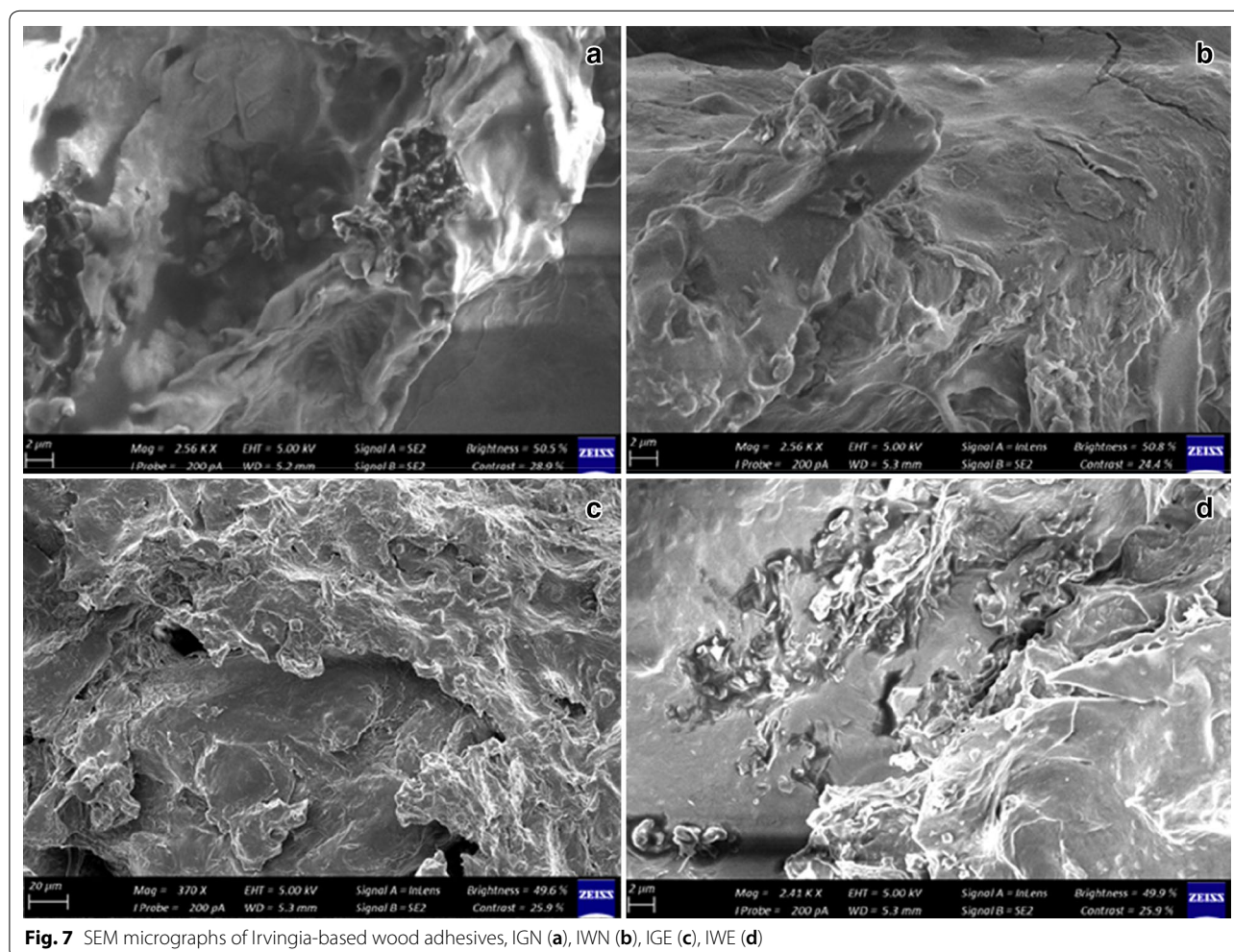
indicating a complex chemical composition. Comparable results were reported in Table 1. After acid/base modification as in the case of IGW/IWC, a significant change in the DTG curve in the region between 240 and 360 °C was observed. In this case, three new DTG<sub>MAX</sub> resolved at 160, 320 and 440 °C. The peak at 160 °C can be ascribed to sodium carboxylate form from the reaction between sodium hydroxide and fatty acid, while the peak at 440 °C could be associated to the decomposition temperature of sugar that resulted from the depolymerisation of the starch by hydrochloric acid and the peak at 320 °C is due to the unreacted protein components.

As indicated on the DTG curve, the decomposition temperature profiles for IGE and IGG/IWG in the 200–400 °C temperature region are very similar and are comparable to their unmodified counterparts except that the content is suppressed by the presence of PE. However, IWE demonstrates major changes in this region with the emergence of a new peak at 340 °C. This could be due to crosslinking effect with the epichlorohydrin modifier.

The dominant peak at 460 °C in both samples is typical of the PE used in the modification. The effect of glyoxal/PE in the case of IGLY enhances peak broadening of the PE and a mark peak shift from 460 to 480 °C was observed. This change was not seen for IWLY.

#### SEM analysis

SEM micrographs of modified and unmodified adhesives are presented in Fig. 7a–d. This analysis was conducted to reveal any morphological changes on the surface properties of modified adhesive samples. It is clearly shown that the smooth surfaces of unmodified Irvingia extracts for both species turned entirely rough after modification with different hardeners. Similar observation was reported by Hosseinpourpia et al. [43]. Furthermore, adhesive granules were coated with coarse films for all modified samples. This may be due to the existence of modifiers, which resulted in possible blending and side reactions between unmodified sample and modifiers. The SEM micrographs established the visual agreement on successful modification of the kernel extracts.

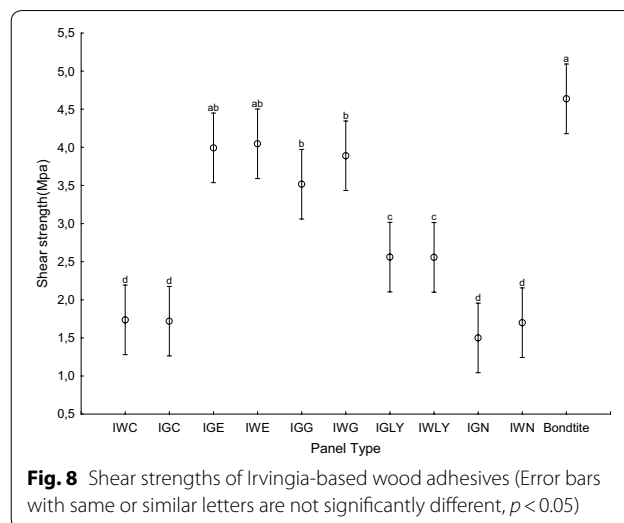


### Energy dispersive spectroscopy (EDS) analysis

From the SEM, characterization of the surface composition of the modified and unmodified adhesive samples was performed using the EDS. The spectral diagram obtained was used to generate elemental composition of the samples, and the means of three random observations are presented in Table 5 for each sample. It was observed that all adhesives contain carbon, nitrogen, magnesium, phosphorus, sulphur, chlorine, calcium and oxygen, while sodium, aluminum, silicon, potassium and iron were only present in some samples. It was obvious that carbon and oxygen were substantially present in all the samples for both species. It was also observed that all the samples have low C/O ratio which ranges between 0.34 and 0.38. This is due to high content of oxygen in all the samples. It is important to note that the C/O ratio refers to general ratios and not necessarily chemically bound in the reactive oxygen intermediates (ROI). This means oxygen can be bound to any of the metals as well and not only to carbon.

### Effect of modification on adhesive shear strength

Shear strength is an important performance criterion of adhesives. Shear strength is applicable in adhesive development, manufacturing quality control, and in materials performance specifications. The mean values of shear strength for the panels made from both modified and unmodified samples are presented in Fig. 8. The adhesive's shear strength varies with modification methods and species. Panels produced with Bondtite 345, which is a commercial adhesive had the highest shear strength of 4.64 MPa while epichlorohydrin modified IW (IWE) had the highest shear strength of 4.05 MPa among the modified samples for both species. This could be due to reinforcing of Irvingia starch granules through crosslinking reaction with epichlorohydrin [24]. According to the results obtained, panels made with Bondtite 345 were



**Fig. 8** Shear strengths of Irvingia-based wood adhesives (Error bars with same or similar letters are not significantly different,  $p < 0.05$ )

not significantly different from the panels produced with epichlorohydrin modified Irvingia adhesives (IWE and IGE), but were significantly different from other samples. Meanwhile, panels produced with IWE and IGE were not significantly different from glutaraldehyde modified samples (IGG and IWG). Acid/base modified adhesives had the lowest shear strength among modified samples for both species: IGC had 1.72 and IWC had 1.74 MPa. The lowest shear strength recorded for modified adhesives is higher than that reported for Whey protein-based wood adhesives [33]. The highest shear strength recorded for modified adhesives, IWE (4.05 MPa) is close to the shear strength value (4.15 MPa) reported by Zhang [19] for grafted starch-based wood adhesive.

The panels produced with unmodified adhesives presented the lowest average values of shear strength (IGN and IWN are 1.5 MPa and 1.7 MPa, respectively); and these values are about 41 (IGN) and 34% (IWN) lower than the shear strength of modified samples with lowest

**Table 5** Elemental composition (%) of unmodified and modified Irvingia-based wood adhesives

Samples	C	N	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	O
IWN	26.97	0.03	–	0.13	–	0.01	0.13	0.07	0.03	–	0.05	0.02	72.29
IGN	26.58	0.10	–	0.26	0.03	0.03	0.31	0.18	0.10	–	0.12	0.02	71.81
IWC	23.54	1.37	8.07	0.19	–	0.06	0.17	0.09	1.37	–	0.08	–	66.14
IGC	20.72	2.47	14.98	0.09	–	0.03	0.12	0.10	2.47	–	0.06	0.06	60.94
IWE	27.10	0.25	–	0.08	–	0.01	0.04	0.03	0.25	–	0.01	0.01	72.37
IGE	27.00	0.15	0.06	0.08	–	0.02	0.02	0.01	0.15	0.15	0.01	–	72.54
IWG	27.02	0.01	0.06	0.13	–	0.01	0.09	0.03	0.01	0.51	0.01	–	72.48
IGG	27.12	0.02	–	0.04	–	0.01	0.02	0.01	0.02	0.53	0.01	–	72.62
IWLY	27.10	0.01	0.03	0.04	0.03	–	0.04	0.01	0.01	0.13	0.01	–	72.58
IGLY	27.24	0.01	–	0.03	–	0.01	0.02	0.01	0.01	–	0.01	–	72.64

C-content values are slightly higher than the actual values. All samples were coated with a thin layer of carbon prior to microscopy

values. There was no significant difference between panels made with acid/base modification (IGC and IWC) and unmodified adhesives (IGN and IWN). It can be inferred that acid/base modification process is not suitable to modify *Irvingia*-based adhesives to improve its strength. The minimum requirement for the characteristic shear strength for panel production for cross layer bond lines according to EN 16352 is 1 MPa [44]. Hence, all panels met the minimum requirements. Based on a one-way analysis of variance (ANOVA) on the shear strength of adhesives in relation to different modification methods and species, the analysis showed that modification methods significantly affected the shear strength, while the shear strength between the species did not differ. Concisely, modified *Irvingia*-based adhesives present good bonding properties.

## Conclusions

This study examined the feasibility of developing an environmental friendly natural wood adhesive synthesized from *Irvingia*-based kernel extracts via a modification process using four selected hardeners and polyethylene as modifiers. TGA and DTG results showed that modified adhesives have low thermal degradation and good thermal stability. DSC results revealed that the curing temperature of all modified samples is in a close range irrespective of species and modification method. FTIR results showed changes in the functional groups of modified samples, as seen in the emergence of new peaks and bands. The effect of the modification was evaluated through the shear strength of plywood bonded with the adhesives and the results indicated that the shear strength of the modified adhesives was significantly improved. Thus, modification of the *Irvingia*-based adhesives resulted in better properties, which contributed to the strength of the adhesives as observed in this study. The main advantage of these modified adhesives is that they do not contain formaldehyde or phenol, both of which are considered potent environmental contaminants.

## Abbreviations

IG: *Irvingia gabonensis*; IW: *Irvingia wombolu*; PE: Polyethylene; FTIR: Fourier transform infrared spectroscopy; DSC: Differential scanning calorimetry; SEM: Scanning electron microscopy; TGA: Thermogravimetric analysis; WHO: World Health Organisation; IS: *Irvingia smithii*; IGF: *Irvingia grandiflora*; IR: *Irvingia robur*; IM: *Irvingia malayana*; PVOH: Polyvinyl alcohol; NMR: Nuclear magnetic resonance; ATR: Attenuated total reflectance; ASTM: American society for testing and materials; RH: Relative humidity; h: Hour; EDS: Energy dispersive spectroscopy; ppm: Part per million; DP: Depolarised; HCl: Hydrochloric acid; NaOH: Sodium hydroxide; PCA: Principal component analysis; DTG: Derivative thermogravimetric; EN: European; IGN: Unmodified *Irvingia gabonensis*; IGC: Acid/base modified *Irvingia gabonensis*; IGE: Epichlorohydrin modified *Irvingia gabonensis*; IGG: Glutaraldehyde modified *Irvingia gabonensis*; IGLY: Glyoxal modified *Irvingia gabonensis*; IWN: Unmodified *Irvingia wombolu*; IWC: Acid/base modified *Irvingia wombolu*; IWE: Epichlorohydrin modified *Irvingia wombolu*; IWG: Glutaraldehyde modified *Irvingia wombolu*; IWLY: Glyoxal modified

*Irvingia wombolu*; C: Carbon; N: Nitrogen; Na: Sodium; Mg: Magnesium; Al: Aluminum; Si: Silicon; P: Phosphorus; S: Sulphur; Cl: Chlorine; K: Potassium; Ca: Calcium; Fe: Iron; O: Oxygen; ROI: Reactive oxygen intermediates.

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## Authors' contributions

AOA and LT conceived the study. All the authors designed and coordinated the experiments. AOA and PSEB performed the experiments and drafted the manuscript. SOA, MM and LT reviewed the manuscript. All authors approved the final manuscript.

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## Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

## Competing interests

The authors declare that they have no competing interests.

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