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RESEARCH ARTICLE

Fiber level catalyst-free oxidative carboxylation enhances physical properties of wood polymer composites

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Abstract

The widespread use of environmentally friendly medium-density fiberboard (MDF) panels as a wood composites is driven by their versatility, affordability, and durability. However, reliance on traditional wood preservatives and modifications raises significant environmental, health, and cost concerns due to harmful chemicals. To address this, we present a one-step nitric acid steam oxidative modification on wood fibers to directly introduce carboxylic acid groups on the surface and eliminate the need for catalysts, organic solvents, or complex multistep procedures often used in traditional methods, such as TEMPO-mediated oxidation. Our multiscale characterization techniques revealed significant changes in the morphology, crystallinity, and surface features of the treated wood fibers, which directly translated to enhanced bulk mechanical properties of the wood composites. Remarkably, the internal bond strength (IBS) of the wood panels increased from 0.27 MPa in untreated panels to 0.89 MPa in panels treated with 5% carboxylated (CA) fibers, suggesting a 3.3-fold enhancement. Additionally, the water uptake of the modified panels was dramatically reduced, with 5% CA-treated panels absorbing only 3.46% compared with 30.38% in unmodified panels, signifying dimensional stability. Furthermore, the curing temperature of the adhesive with CA-treated fibers was lowered by 50°C without reducing composite strength, highlighting significant energy savings. Also, formaldehyde emissions from the 10% CA-modified panels were reduced by 14.82% compared with unmodified panels, aligning with regulatory standards. These findings demonstrate that catalyst-free oxidation enhances adhesive bonding and mechanical performance in wood composites while providing an eco-friendly method for lignocellulosic fiber modification.

Highlights

- Catalyst-free, one-step oxidation of wood fibers with nitric acid steam.
- Carboxylation greatly enhanced fiber bonding with adhesives.
- Modified fibers improved panel strength and reduced water absorption.

- Lower curing temperature offers energy savings in production.

KEYWORDS
adhesive, carboxylation, lignocellulose, wood composites, wood modification

1 | INTRODUCTION

Wood panels have gained widespread recognition for their versatility, affordability, and eco-friendly nature. Over the years, significant efforts have been made to enhance their strength and resilience to harsh environmental conditions by improving both the mechanical and chemical aspects of their performance by using protective treatments, including biocides, coatings, or water repellents. While these treatments improve the lifespan of wood products, they face some environmental challenges because of toxic chemcials.[1] Thus, there have been regulations against biocidal systems to remove and ban them from the European Market based on the Biocidal Product Regulation.[2] Moreover, the development of wood products, including particleboard, medium-density fiberboard (MDF), and plywood, depends highly on the use of formaldehyde-based adhesives due to their high reactivity, chemical adaptability, and cost-effectiveness.[3,4] Formaldehyde is a volatile organic compound (VOC) and can be slowly released into the ambient from adhesives, raising concerns due to its potential adverse effects on indoor air quality and human health. Strict regulations, like European E emission classes, US CARB standards, and Japanese F*** and F**** classes,[5,6] have been enforced to limit formaldehyde emissions; therefore, developing new formulations with low-emission or completely formaldehyde-free and environmentally friendly solutions to protect wood without sacrificing the mechanical properties and dimensional stability of the wood products is urgently needed.[5,7] Meanwhile, polymer adhesives like diphenylmethane diisocyanate (pMDI), a formaldehyde-free adhesive, have gained increasing attention due to their exceptional reactivity, curing characteristics, water resistance, and bonding properties. However, challenges with pMDI are not related to its performance but rather to its practical application and cost. This cost disparity[8] coupled with its potential health risks to humans makes pMDI less attractive to industries prioritizing cost-efficiency, despite its superior properties and environmental benefits.[9,10] The primary factor contributing to these challenges is the high reactivity of the isocyanate groups in pMDI compared with the UF resins. While this reactivity is beneficial for rapid curing, it creates significant issues during the manufacturing process, such as a tendency to stick to press surfaces during hot-pressing operations, complicating production, and increasing costs.[11] Additionally, pMDI has limited effectiveness in filling irregular spaces, which restricts its performance in applications requiring a continuous and uniform bondline.[12,13] Furthermore, pMDI's low molecular weight contributes to excessive penetration into the porous structure of wood substrates. While some degree of penetration is necessary to achieve mechanical interlocking, overpenetration leaves insufficient adhesive at the bondline, resulting in a weak and discontinuous interface compared with UF-resin systems. This reduces the strength and durability of plywood and laminated veneer lumber, particularly in applications that demand uniform adhesive coverage.[13] Addressing these issues often requires complex modifications, such as using organosolvent,[14] fillers or extenders[12,15] to the adhesive or processing methods, which can increase both costs and operational complexity.[6,12,16–21] Thus, UF resins, despite formaldehyde emissions and the presence of less reactive groups, remain a cost-effective and efficient option for achieving consistent fiber bonding in wood composites.

To address the weak bonding between urea-formaldehyde and wood fibers, wood modification techniques have emerged as a promising approach to improve the bonding of lignocellulosic fibers with adhesive, thus significantly reducing the use of formaldehyde. Various chemical modification techniques, including etherification, oxidation, esterification, and carboxymethylation, have been demonstrated to oxidize hydroxyl groups from cellulose derived from diverse biomass sources.[22,23]

Among other functional groups, carboxylic acid groups enhance self-binding and fiber interactions, making composites more resilient. The hydrophilic surface of modified wood fibers improves the curing process with urea-formaldehyde adhesives, enhancing wetting and promoting uniform adhesive distribution. This leads to stronger intermolecular forces between fibers and adhesives, improving chemical compatibility.[24] Importantly, the modified hydrophilic surface provides greater stability without the need for extra crosslinking agents compared with the hydrophobic surfaces due to superior mechanical interlocks, molecular-level interactions, and secondary force interactions.[25] However, typical pretreatment methods to create the carboxylic acid groups involve solvent treatment, alkali pretreatment, and bleaching of the wood chips or fibers. The tetramethyl pentahydropyridine oxide (TEMPO) approach has been widely used to selectively oxidize the primary hydroxyl groups ($—CH_2OH$) on the cellulose chains to carboxylic acid groups (—COOH). The methods target primarily the cellulose components with a small effect on lignin and hemicellulose, requiring many pretreatment procedures for cellulose extraction from untreated biomass.[25–28]

TEMPO is costly and poses economic challenges for large-scale industrial use due to its multistep process and reliance on radical-generating chemicals like TEMPO reagents, sodium hypochlorite, and bromide, involved in the process. Additionally, the excess chemical use generates significant amounts of waste byproducts, thus limiting its sustainability.

In this work, we focus on the surface oxidation of wood fibers through a steam oxidative treatment, particularly employing nitric acid, to enhance the adhesion and interfacial properties within wood fiber-reinforced resin composites. Unlike the traditional methods, this approach offers a practical and cost-effective solution to improve interfacial wettability without compromising the mechanical integrity of wood fibers.

The nitro-oxidation process (NOP) has been used to isolate cellulose nanofibers (CNF) from various biomass sources, simplifying wood pulping and oxidative modification of cellulose by using only nitric acid and sodium nitrite.[29–31] A gas-phase NO_2 treatment further oxidizes delignified fibers, achieving high carboxylic acid group concentrations (1.31–1.45 mmol/g), comparable to TEMPO-mediated oxidation.[32] This process enables notably oxygen-containing functional groups such as hydroxyl, carbonyl, ketones, and carboxylic acids. The key distinction of our study from other carboxylation processes lies in achieving comparable and enhanced wood composite properties, such as increased internal bonding strength (IBS) and dimensional stability. This was achieved through a straightforward nitric acid modification method applied directly to wood fibers. This approach also reduces curing temperature and energy demands, setting our method apart from traditional, more complex, and multistep oxidation techniques. Using multiscale characterization techniques, our study shows that using the straightforward and one-step nitric acid steam method can be an alternative to conventional oxidation methods by directly forming carboxylated (CA'ed) wood fibers and reducing environmental impact by utilizing a controlled, closed system that captures NO_2 fumes, thereby minimizing environmental and exposure risks. The treatment influenced the effect of treatment on the morphology, crystallinity, and surface features of individual wood fibers, which reflect on the bulk mechanical properties of the wood composites. The internal bond strength (IBS) of the wood was significantly improved from 0.27 MPa in the unmodified wood panel to 0.89 MPa in the wood panel treated with 5% CA, highlighting a 3.3-times increase compared with the untreated panel and other similar studies. In terms of water uptake over 2 h, the unmodified wood fiber panel absorbed 30.38%, while the modified panels treated with 5% CA and 10% CA absorbed only 3.46% and 5.48%, respectively. Most importantly, the curing temperature of the resin can be decreased by $\approx 50^\circ C$ without sacrificing the mechanical performance of the composites, which can lead to significant energy savings. Furthermore, the modification of wood fibers also contributed to a reduction in formaldehyde emissions. Panels made from unmodified fibers exhibited a formaldehyde emission of 11.40 ± 0.57 mg/100 g, while panels incorporating 10% CA-modified fibers showed a slightly reduced formaldehyde emission of 9.71 ± 0.021 mg/100 g, corresponding to a reduction of approximately 14.82%. The unique properties achieved through our carboxylation process, alongside the promising performance results, suggest that this modified wood fiber approach holds strong potential for enhancing IBS and dimensional stability in wood composites.

2 | EXPERIMENTAL METHODS

2.1 | Materials

The red pine wood fibers used in this study were supplied by Kastamonu Integrated Wood Industry (KEAS, İstanbul, Turkey). The experimental chemicals included nitric acid (HNO_3, 65 wt%), (EMSURE® analytical grade) were purchased from (Sigma-Aldrich Chemie, Germany) for chemical modifications. The UF resins (1.22 M) widely used in particleboard production as binding agents were provided by KEAS (İstanbul, Turkey). The preparation of laboratory-scale particleboards, as well as testing for mechanical properties and formaldehyde emissions, was carried out using the advanced facilities available at KEAS (İstanbul, Turkey). For formaldehyde emission tests, toluene (≥99.9% purity, GC, EMSURE®), acetylacetone (≥99.0% purity, EMSURE® analytical grade) and ammonium acetate (≥98.0%, ACS reagent grade, Sigma-Aldrich) were used as reagents.

2.2 | Chemical treatment of wood fibers

Carboxylation process was carried out on wood fibers using the following procedure. Initially, 200 mL of nitric acid underwent thermal decomposition at a temperature of 130°C in a round bottom flask placed in an oil bath, and then the formed gas was passed through the

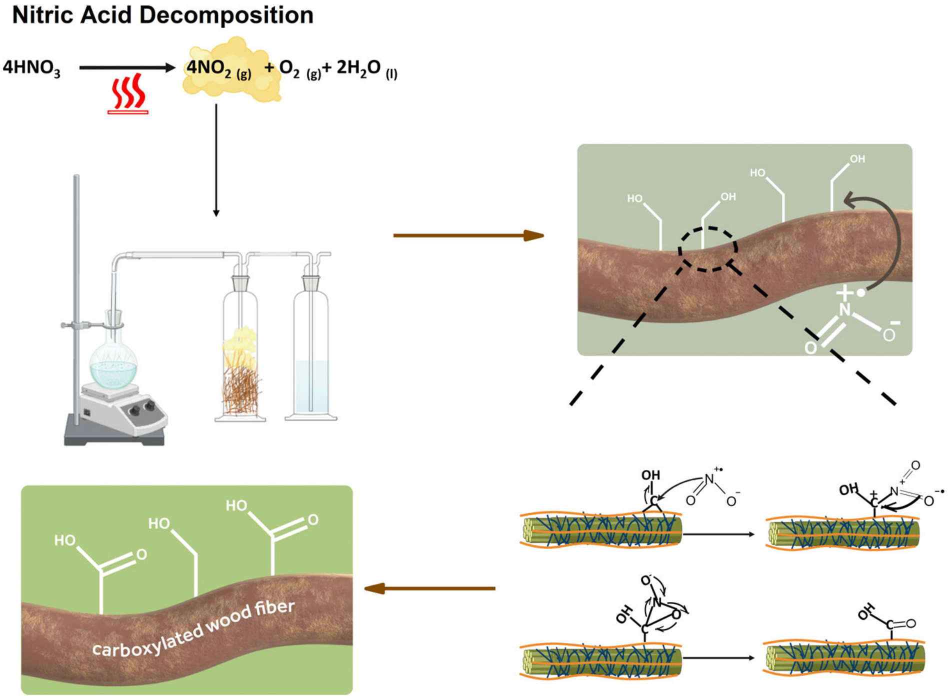

FIGURE 1 Schematic illustration of nitric acid steam treatment of wood fiber and the reaction mechanism between nitrogen dioxide and C—C bonds in the wood structure.

gas washing bottle containing 10 g of wood fibers, as shown in Figure 1 for different durations (15, 30, and 60 min). Then, the NO_2 gas generated was transferred into a separate water-filled wash bottle, where it was dissolved and converted back into nitric acid. This method utilizes nitric acid within a carefully controlled, closed system that prevents the release of NO_2 fumes, minimizing environmental impact, exposure, and improved safety. Finally, the reacted wood fibers were rinsed with deionized water under vacuum filtration until the filtrate reached a neutral pH to make sure there was no nitric acid left on the fibers. The washed modified fibers were dried at 50°C for 1 day. These modified fibers were ready to be analyzed further and used in wood-panel production.

2.3 | Characterization of nitric acid steam-treated wood fibers

2.3.1 | Structural analysis

Before all measurements, samples of wood fibers were dried at 50°C overnight to ensure consistent results and remove the moisture, and each test was run three times to make sure the results were consistent and reproducible.

To analyze the chemical modifications from carboxylation of hydroxyl groups on the fibers, Fourier-transform infrared (FTIR) spectroscopy was used with a Thermo Scientific iS10 FTIR (Thermo Fisher Scientific, USA) between 400 and 4000 cm^{-1} with 64 scans at a spectral resolution of 4 cm^{-1}, and the data were processed in transmittance mode using Origin Pro software.

The crystallinity of the modified fibers was determined through X-ray diffraction (XRD) analysis using a Bruker D2 Phaser x-ray diffractometer (Bruker Corporation, USA) with a Cu Kα radiation source (wavelength of 1.5406 Å). The samples were positioned centrally in the holder, and then, diffraction data were collected at room temperature over a 2θ range of 10°–80°with a scanning rate of 1.0°/min and a sampling interval of 0.05°. Then, the data were processed using Origin Pro software.

X-ray photoelectron spectroscopy (XPS) measurements were conducted utilizing a Thermo K-Alpha x-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) under ultrahigh vacuum conditions. The binding energies in the XPS data were calibrated based on the C—C bond in the C 1s region at 284.6 eV by using Avantage software (ver. 6.6.0, Thermo Fisher Scientific).

The surface morphology of raw and nitric acid steam-modified pine needles was observed using a Zeiss Ultra Plus field emission scanning electron microscope (FESEM, Zeiss Ultra Plus, Germany). Before analysis, the samples were uniformly gold-coated for 20 s using a sputter coater. Imaging was conducted under high vacuum conditions with an accelerating voltage of 5 kV.

The contact angle of fibers was determined using the meniscus method with an Attension Theta Lite optical tensiometer (Biolin Scientific, Finland). In this process, individual wood fibers were submerged in distilled water. As the sample was pulled out from the liquid, a meniscus took shape, and the angles were recorded from the right and left angles. Deionized water, with a surface tension of 72.6 ± 0.1 mN/m, was utilized in all experiments at a temperature of approximately 22°C to ensure accurate and reproducible results.

UV–visible spectra of the carboxylated wood fibers were recorded in the wavelength range of 200–700 nm using a Shimadzu UV-3600 UV–VIS–NIR spectrophotometer (Shimadzu Corporation, Japan) in reflectance mode at room temperature with a sampling interval of 1 nm.

2.3.2 | Thermal analysis

Thermogravimetric analysis (TGA/DTG) was performed on the samples using a (Mettler Toledo, Turkey) under a nitrogen atmosphere with a flow rate of (30 mL/min) from 25 to 600°C at a heating rate of 10°C/min, followed by an additional heating step from 600 to 800°C under an oxygen atmosphere at 10°C/min.

The DSC 1 instrument (Mettler Toledo DSC 3+, USA) was utilized to investigate the curing processes through the differential scanning calorimetry (DSC) method. The wood fibers were initially mixed with urea-formaldehyde adhesives, with the same binder-to-fiber ratio of 11%, which matched the quantity required for panel production. The prepared samples were then carefully positioned between an aluminum cup and lid to securely contain them and prevent deformation under pressure. The samples were sealed tightly to keep water inside during the testing process, preventing any loss of water content. Then, the sealed container was placed into a specialized machine, and nitrogen gas with a flow rate of (30 mL/min) was used to increase the pressure inside to 1.6 MPa. This helped control the temperature range for water vapor and prevent water from evaporating while the samples were heated. The samples were gradually heated at a rate of 10°C/min, ranging from 20 to 200°C.

2.4 | MDF production

Figure S4 illustrates the production parameters and process for MDF. Panels including (i) unmodified fibers, (ii) 5 wt% carboxylated fibers mixed with raw fibers, (iii) 10 wt% carboxylated fibers mixed with raw fibers, and lastly (iv) 100% carboxylated fibers (not mixed with raw fibers) were separately prepared to investigate the modification effect on MDF. The solid content of the urea-formaldehyde resin is 65% by weight without using any paraffin or other water-repellent chemicals. The resin solution, at a concentration of 11% by weight of fibers, was applied through spraying. The bonded fibers were manually formed into mats by placing them within a wooden frame (200 × 200 × 8 mm^3). This process was repeated three times for each treatment. In the final step, the pine fiber mats were subjected to hot pressing at a pressure of 80 bar and a temperature of 200°C for 4 min. This process was aimed at promoting the curing of the resin, ensuring the fibers were firmly bonded. After pressing, the panels were allowed to cool gradually at room temperature for 24 h.

The physical properties of the wood panels were assessed by measuring the IBS under dry conditions with a ZwickRoell testing machine (Model Z010 ZwickRoell, Germany) equipped with a 10 kN load cell as well as thickness swelling (TS). After 2 h and water absorption (WA) after 24 h were based on the European Standard (EN) methods.

The formaldehyde content in modified wood panels, specifically those treated with nitric acid, was determined according to the European Norm (EN 12460–5)[33] using the perforator method. In this process, the panels were first cut into small pieces of approximately 110 ± 0.01 g with the size of 25 mm × 25 mm for uniform extraction. They were immersed in 600 mL of toluene and boiled at 200°C for 2 h in reflux, with a rate of 70–90 drops per minute, in a round-bottom flask attached to a perforator setup, which included 1000 mL of distilled water. During the extraction, the formaldehyde gas released from the panels was directed through the condenser and collected in the gas absorption bulb, which was filled with 100 mL of distilled water. After the 2-h extraction was complete, the water was cooled to room temperature. The water with extract collected in the absorption bulb of the gas absorption equipment was transferred into the flask, and distilled water was added to bring the total volume of the solution to 2000 mL. The formaldehyde content was measured spectrophotometrically using the acetylacetone method based on the EN ISO 12460-5 standard. First, 4 mL of acetylacetone was diluted in 1000 mL of distilled water, and 200 g of ammonium acetate was dissolved in 1000 mL of distilled water separately.[33] Then, 10 mL of the extract from the 2000 mL solution was mixed with 10 mL each of the acetylacetone and ammonium acetate solutions in a flask. The mixture was shaken, heated to 60°C, and then cooled to room temperature for 1 h, while protecting it from sunlight. The solution color turned yellowish. The solution was then transferred to a formaldehyde test cuvette (HACH LCK 325, UK), and the formaldehyde concentration was measured using a DR 2800 spectrophotometer (HACH, UK) at a wavelength of 412 nm. The results were repeated two times and are reported as mg of formaldehyde per 100 g of oven-dry board.

3 | RESULTS AND DISCUSSION

3.1 | Investigation of unmodified wood fibers

The structural and morphological properties of unmodified fibers were investigated using an optical microscope (Figure S1). Raw fibers analyzed with Image J software had lengths of 4.042 ± 0.70 mm and thicknesses of 0.1368 ± 0.673 mm. After modifications for 15, 30, and 60 min, average sizes were 3.17 ± 0.68 mm (thickness 0.0686 ± 0.0035 mm), 1.70 ± 0.30 mm (thickness 0.0397 ± 0.0044 mm), and 0.47 ± 0.15 mm (thickness 0.0243 ± 0.0062 mm), respectively. The monotonic reduction in fiber size is due to the partial disintegration of fiber bundles during modification. Notably, the 60-min modification showed significant size reduction with a more uniform size distribution compared with shorter durations. Also, raw fibers have lower aspect ratios than those treated for 15 and 30 min, while the 60-min treatment showed the lowest aspect ratio. Optimal aspect ratios are crucial for maximizing fiber reinforcement, particularly in strong fiber-matrix bonds and lower fiber strength,[34] therefore, the fibers modified for 15 and 30 min, with their higher aspect ratios, can provide better reinforcement for wood panels, whereas 60 min modification deteriorates.

3.2 | Carboxylation of the pine wood fibers

First, the effect of the treatment time with nitric acid (65 wt%) steam was studied by treating 20 g of fibers for 15, 30, and 60 min at a temperature of 130°C (see experimental section and Figure 1 for details). This reaction occurs after the thermal decomposition of nitric acid at higher temperatures. The nitric acid functionalization process is primarily based on the thermal decomposition of nitric acid. The reaction proceeds via a simple oxidative process utilizing nitric acid, specifically applied at its decomposition temperature (130°C) producing NO_2 gas. Under nitro-oxidation conditions, the reaction is initiated as nitro species (e.g., NO_2 or NO_3) can attack the carbon atom of the primary alcohol on the surface of the wood fiber, forming a positively charged intermediate carbon atom. In the second step, the oxygen atom on the nitrogen dioxide attacks the carbon atom in the same intermediate, resulting in the carboxylic acid group. Subsequent substitution reactions and rearrangements, coupled with the formation of oxidation, introduce carbonyl or carboxylic acid groups into the lignin structure. After that, the excess acid was washed with deionized water until the pH became neutral. The schematic diagram in Figure 1 illustrates how the application of nitric acid steam modifies the pine wood fiber, providing a visual representation of the introduced nitro groups and the resulting structural changes in each component. Additionally, the different reaction times were tested to investigate the increment in the carboxylic acid content and change in the chemical and morphological structure.

The carboxylation process involves the introduction of carboxylic acid groups onto the wood fibers, as confirmed by the FTIR (see Figure 2). The changes in the peak intensity of the carbonyl group of carboxylic acids, formed by testing different reaction times, were observed around 1720 cm^{-1}. The absence of the carbonyl group at 1720 cm^{-1} in the raw fibers, compared with the modified fibers, is due to the C═O bond in lignin being formed and subsequently cleaved during the carboxylation process, which confirms the successful carboxylation of the fibers. Additionally, the peak around 1507 cm^{-1} is associated with the aromatic C─O of lignin.[35,36] The peak at 1507 cm^{-1} is often associated with the aromatic ring stretching vibrations (C═C) in lignin. When the wood fibers are treated with HNO_3 gas, the oxidation process leads to the modification of lignin mainly. As a result, the intensity of this peak is expected to decrease and shift due to the alteration of the lignin structure. The peak at

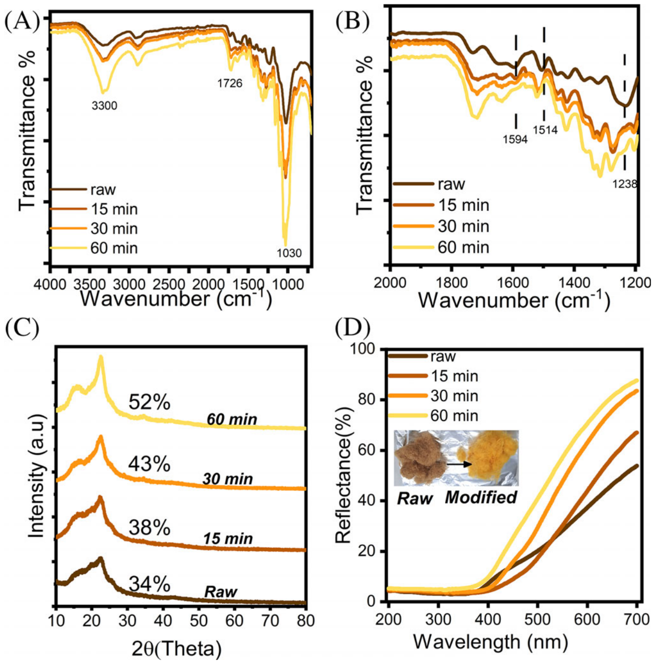

FIGURE 2 (A) Fourier-transform infrared spectroscopy (FTIR) data of raw, 15, 30, and 60 min CA'ed modified fiber and (B) the same spectra in the wavenumber range of 1200–2000 cm^{-1}, respectively. (C) X-ray diffraction (XRD) data of raw fiber, 15 min modified fiber, 30 min modified fiber, and 60 min modified fiber and (D) UV–Vis reflectance results for raw, 15, 30, and 60 min CA'ed modified fiber.

1240 cm^{-1} is typically related to $C{=}O$ and $C{-}O$ present in the hemicellulose component.[29,31] As the wood fibers undergo oxidation with NO_2, these linkages are likely affected, leading to the cleavage of aryl ether bonds in hemicellulose. The decrease in intensity of this peak reflects the removal of the hemicellulose. Even if the intensities decrease, the peak positions might change because of the introduction of oxygen-containing groups or structural alterations. This could explain the shift observed in FTIR data (in Figure 2A,B). The peaks around 1106 and 1317 cm^{-1} corresponding to $C{-}O$ and CH_2 vibrations in crystalline and amorphous cellulose, respectively, were found to increase with increasing oxidation time,[36] due to a free fraction of cellulose after the modification with nitric acid vapor. Particularly, breaking the hydroxyl groups of lignin and hemicellulose could lead to increased cellulose fraction and the peak intensities in the bands between 1317 and 1106 cm^{-1} in Figure 2B.

As the reaction time increases, the structure becomes more hydrophilic as evidenced by a higher intensity of OH stretching at 3300 cm^{-1}, resulting from the breaking of intramolecular hydrogen bonds during the reaction. The removal of hemicellulose, lignin, and extractive substances increased relative to the modification time, leading to a relative increase in cellulose content and, thus, crystallinity. The XRD patterns in Figure 2C show the peaks at $2\theta = 16^\circ$, 22.2°, and 34.4° (corresponding to cellulose I structure) becoming more pronounced, resulting in a monotonic increase in the degree of crystallinity with modification time (34.4%, 38.4%, 43.0%, and 52.0% for raw, 15, 30, and 60 min CA'ed fiber, respectively).

The modification of the wood fibers was determined by visual assessment using the UV–vis spectra in Figure 2D. The color of the wood gets lighter as the treatment time increases. This can be explained by the presence of chromophores in the lignin structure. The strength of certain chemical groups ($-OH$, called auxochromes) in the lignin structure, which are responsible for certain color-related properties, decreases during oxidation with nitric acid steam. This reduction in auxochromes affects another set of groups (chromophores, characterized by $C{=}O$ double bonds) that absorb ultraviolet (UV) radiation.[37] As a result of this steam treatment, the lignin structure undergoes degradation, leading to a lightening of color and altering how wood fibers reflect light in the visible spectrum. Thus, oxidation induces changes in the chemical composition of lignin, weakening its ability to absorb UV radiation. This process, in turn, affects the overall color of the wood fibers by diminishing the intensity of specific chemical groups responsible for coloration. The consequence is a lightening of the wood fibers, making them appear less colored. Additionally, the modified lignin structure influences how these fibers interact with light in the visible range, altering their reflectance properties. This can be advantageous with a more stable color response of wood fibers to light, especially in the visible spectrum. This enhanced light stability is valuable for maintaining the intended color of wood panels over time, preventing undesired fading or discoloration due to exposure to environmental factors.

The structure of the modified wood fibers was examined through SEM microscopy images. Figure 3A shows the surface of the unmodified wood, highlighting the open pit structures present. These pits play an important role in facilitating the water flow radially between neighboring fibers through diffusion. It is important to note that these pits have a semi-permeable, membrane-like surface that allows water to pass through wood inner structure. These pores are particularly important in the production of composite materials as the binding agents can effectively diffuse into the fibers through these pits and effectively fill the hollow fibers. This mimics the natural transport of water in plants, highlighting the intricate contribution of these structural features to the functionality of wood fibers in composite material applications.[38,39] In this study, after a 15-min treatment (Figure 3B), we observe the pits on the tracheid walls (in some cases partially) closed. This closure acts like a barrier, preventing the diffusion of excessive adhesive inside of the fibers. Thus, the closed pits act as gateways

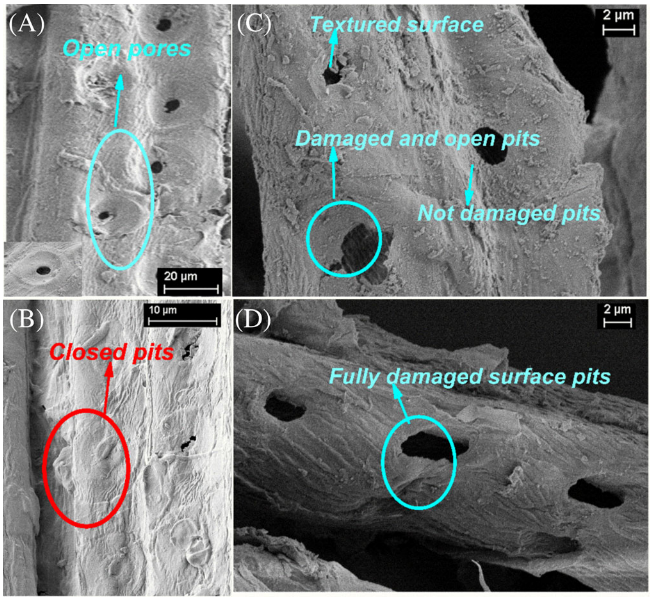

FIGURE 3 (A) Unmodified wood fibers with open pits, (B) 15 min modified wood fibers with closed pits and irregulated wood fibers, (C) 30 min modified wood fiber with damaged pits and surface, and (D) 60 min modified wood fibers with fully damaged and open pits.

controlling how much adhesive can get into. This locking mechanism plays a crucial role in determining the physical properties of wood composite panels. As the treatment progresses toward 30 min, NO_2 gas continues to react with the fibers, potentially penetrating deeper into the material. This resulted in more pronounced surface roughness as compared with the 15-min stage (Figure 3C). More importantly, the pits become more apparent, and the fiber surface exhibits signs of partially damaged areas or etching. Increased chemical activity might lead to the removal of more surface layers, exposing the internal structure of the fibers. The overall trend is toward increased surface damage and roughness with prolonged nitric acid steam treatment. While the carboxylation is increased in 30-min treated fibers and can favor interaction with the adhesive at the surface, the reopened pores allow adhesive to fill in the fibers, thus, reducing the crosslinking density between the fibers. For 60-min treated fiber, the surface damage was notably greater, and the inner layers of the cell wall are even noticeable through the alignment of the cellulose microfibrils (Figure 3D). The size reductions became more evident as shown in Figure S2, leading to highly brittle fibers, accompanied by a reduction in overall fiber dimensions. Consequently, considering the partial closure of the pits after a short treatment time with little surface damage, the panels were produced with fibers modified for 15 min as discussed in Section 3.3.

In addition to surface morphology, we investigated the surface chemistry characteristics of the unmodified and modified wood fibers using XPS (see in Figure 4). The binding energy observed in the C1s* peak can be divided into four distinct carbon species, denoted as C1, C2, C3, and C4. C1 represents carbon atoms attached to hydrogen or carbon atoms (C—H or C—C), typically observed at 284.5 eV. C2 corresponds to carbon atoms bonded to one oxygen atom, such as in C—O or C═O groups at 285.79 eV, C3 is associated with carbon atoms connected to two noncarbonyl oxygen atoms, as in ester or ether linkages (—C—O—C—) at 287.13 eV. Finally, C4 corresponds to carbon atoms linked to both carbonyl and noncarbonyl oxygen atoms (O═C—O—) at 288.91 eV.

When comparing modified fiber with unmodified wood fibers, there was a decrease in C1. C1 is found mainly in lignin and extractives, so the decrease in C1 was likely caused by breaking the bond in the C—C bond in the structure of lignin and the formation of oxygen-containing structures like carboxyl structures because both oxygen content increased in the carbon structures C2 (—C—O) and C4 (O═C—O—). While for 60 min modification, C4 (O═C—O—) decreased, the formation of C2 (—C—O) or (—C═O) groups increased. This change can be related to the degradation of lignin and extractives after a longer modification time, so the formed carboxylic acid groups can be decreased. Another reason can be due to the existing high oxidation state; additional oxidation causes the removal of the carboxyl carbon in the form of carbon dioxide. Depending on the reaction parameters, the oxidation state of the remaining organic structure may decrease or remain unchanged. Additionally, these findings align with the results of the FTIR analysis.[40–43] Furthermore, it was found that the O/C ratio of unmodified wood fibers was 0.29, which increased to 0.48, 0.51, and 0.59 for 15, 30, and 60 min modified fibers, respectively (Table 1). This confirmed that oxygen-containing structures on the surface were increased after modification.

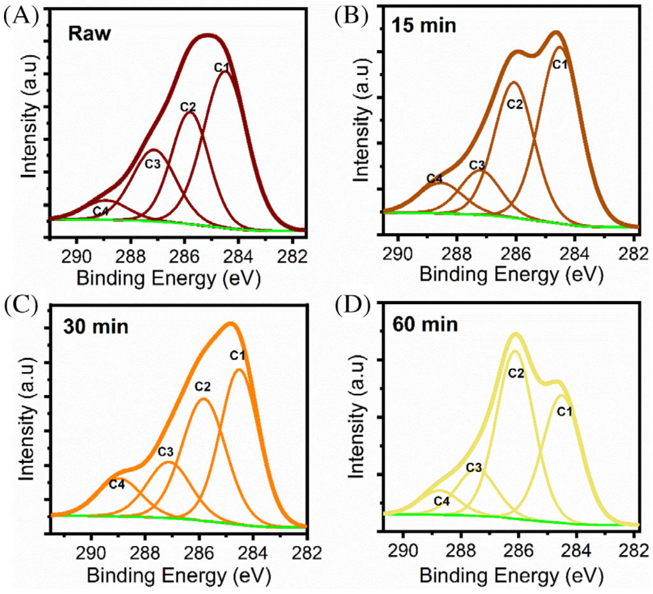

FIGURE 4 High-resolution x-ray photoelectron spectroscopy spectra of (A) wood fibers, (B) 15 min CA'ed wood fibers, (C) 30 min CA'ed wood fibers, and (D) 60 min CA'ed wood fibers. Carbon components: C1: —C—H or —C—C; C2: —C—O or —C═O; C3: —C—O—C—; C4: O═C—O— groups.

The change in surface chemistry reflects also on the thermal stability of the CA'ed wood fibers as well as hydrophilicity. Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) curves are presented in Figure 5A,B. The essential parameters of the pyrolysis process, including onset degradation temperature (T_{onset}), maximum degradation temperature (T_{max}), weight loss, and char residues, were characterized and presented in Table S1. The results of TGA showed that the decomposition of hemicellulose, cellulose, and lignin occurs over different temperature ranges; generally, hemicellulose decomposes at a lower temperature range (220–315°C) than cellulose (300–400°C), while lignin decomposes over a broad range of temperatures (150–

TABLE 1 Surface chemistry analysis of wood fibers by x-ray photoelectron spectroscopy.

Sample		% C component (binding energy, eV)				
		C1	**C2**	**C3**	**C4**	**O/C ratio**
Untreated		35.13 (284.5)	21.53 (285.79)	16.07 (287.13)	4.38 (288.91)	0.29
Modified	15 min	30.85 (284.5)	22.95 (286.06)	7.58 (287.2)	5.8 (288.55)	0.48
	30 min	25.51 (284.5)	22.86 (285.82)	10.5 (287.11)	7.09 (288.95)	0.51
	60 min	21.93 (284.5)	28.17 (286.12)	8.21 (287.46)	4.23 (288.75)	0.59

Note: Carbon components belong to C1: —C—H or —C—C; C2: —C—O or —C═O; C3: —C—O—C—; C4: O═C—O groups.

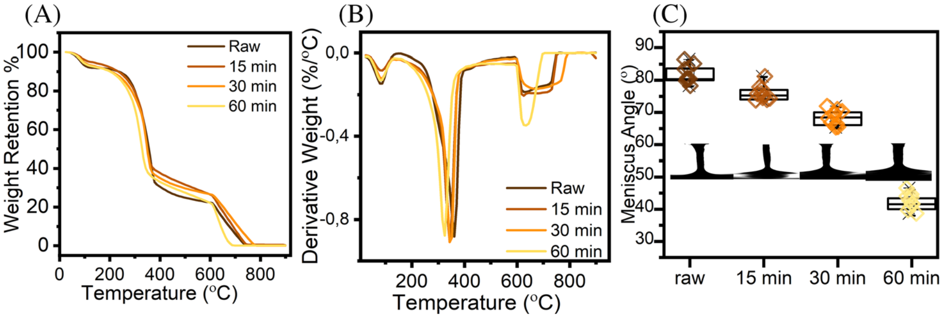

FIGURE 5 (A) Thermogravimetric analysis of wood fibers with raw, 15-min, 30-min, and 60-min CA'ed wood fibers, (B) DTGA analysis of wood fibers with raw, 15-min, 30-min, and 60-min CA'ed wood fibers, and (C) Meniscus angles of raw, 15-min, 30-min, and 60-min CA'ed fibers, respectively.

900°C).[44] After the carboxylation of the wood fiber, the weight loss of unmodified fiber decreased from 65.43 wt% to 59.31% (for 15 min), 59.96% (for 30 min), and 62.04% (for 60 min) in the temperature range of 200–450°C. Interestingly, the 15-min treated sample resulted in less weight loss, possibly due to less surface damage and closure of the pits preventing heat and mass transport toward the fibers by forming a continuous char layer. Increasing treatment time reverses the effect, and the result for the 60-min treatment approaches the value obtained for the unmodified fibers. Additionally, the onset temperature of the 60 min treated started at a lower temperature compared with the unmodified samples, due to the removal of the lignin component promoting the breakdown of cellulose and hemicellulose components. After 600°C, the gas was switched to oxygen to complete the burning process. The derivative weight loss data for this region show the rapid oxidative degradation of the 60-min treated sample due to its thinner fiber morphology and higher cellulose content.

The interaction of individual fibers with water is also important as the adhesives are water-based. Figure 5C and Figure S3 display the meniscus angle analysis. The wetting angles with water demonstrated a notable range, averaging around 81.65° for raw fiber, 75.69° for 15 min modified fiber, 68.11° for 30 min modified fiber, and 41.74° for 60 min modified fiber. The large meniscus angle for the untreated wood fibers indicates a weak attraction to water, suggesting their less hydrophilic nature due to lignin content. On the other extreme, 60-min CA'ed wood fibers, with their lowest meniscus angle, display a notable hydrophilic character due to carboxylation as well as exposure of cellulose on the surface. The meniscus angle of 15 and 30 min modified fibers displays an intermediate response. Besides the immediate effect on the mechanical properties of the composite panels we discuss in the next section, incorporating hydrophilic fibers can help control humidity levels by absorbing excess moisture from the surroundings, contributing to a more stable and comfortable indoor environment.

In summary, we detailed the modification involving an oxidative process to introduce carboxylic acid groups to fibers through nitric acid treatment and subsequent reaction of the modified fibers with UF resin. The esterification process through the reaction between the carboxylic acid groups of the fibers and the hydroxyl groups of the resin precisely altered the fibers, reducing open pits and hydroxyl content. The resulting changes in the nitric acid-treated fibers established stronger covalent bonds between the fibers and the resin, exceeding the strength of hydrogen bonding. This suggests that the covalent attachment of nitric acid-treated fibers containing carboxylic acid groups to the resin serves as a modification method, enhancing strength and introducing hydrophilic characteristics. This not only improves adhesion but also addresses challenges related to cost, energy consumption, and potential fiber strength loss. This innovative approach precisely targets the surface chemistry of wood fibers, promoting enhanced adhesion and compatibility with synthetic resins.

3.3 | Physical properties of modified fiberboards

Our one-step method of modification showed that fibers with carboxylic acid groups resulted in a stronger structure and more resilient bonds compared with untreated fibers. The panels were made from three types of fiber mixtures: 100% unmodified fibers, 5% CA'ed fibers mixed with 95% unmodified fibers, and 10% CA'ed fibers mixed with 90% unmodified fibers, which were tested in terms of their dimensional stability and water uptake. We chose 15-min treated fibers to mix with raw fibers since they are effectively carboxylated without surface damage (as in 30-min treatment) or disintegration (as in 60-min treatment), and the pits are partially closed (see the above sections for details). The process of composite panel production with UF resin is given in Section 2 and Data S1. To assess the impact of the modification on the performance of wood products, the density, IBS, TS, and WA were measured over periods of 2 and 24 h.

The 2-h and 24-h WA and TS test results from the panels composed of 5% and 10% CA'ed fibers (Figure 6A,B) show significant reduction when modified fibers are used. The improved dimensional stability can be related to the closed pits of fibers after modification[36] (as schematically shown in the reaction mechanism in Figure 7). WA in the wood fibers unfolds in two stages: Water first binds to the cell walls and middle lamella via hydrogen bonds with hydroxyl groups (—OH), and then free water occupies micropores and macropores within cell walls, filling voids and being retained by capillary forces. When water vapor permeates and absorbs into cell walls and middle lamella, the cell swells. As a result, bound water saturates the cell wall and middle lamella until the water saturation point of plant cells, typically around 20%–40% for wood cells, is reached. Subsequently, cellular cavities (lumens and porosities) achieve complete saturation because they are filled by free water.[36,45] Thus, the closure of the pits in the modified fibers prevents bulk water from diffusing into the interior of the fiber and the panels.

Another reason for lower water uptake and TS can be the carboxylic acid groups on the modified wood surfaces, which introduce extra reactive sites through the Fischer esterification.[46] The formation of covalent bonds between the fibers and urea-formaldehyde resin results in stronger binding with the resin. This results in a slower water uptake in the panels produced from the 5% and 10% CA'ed fibers, whereas in unmodified fibers, the WA is fast and possibly reaches closer to the saturation

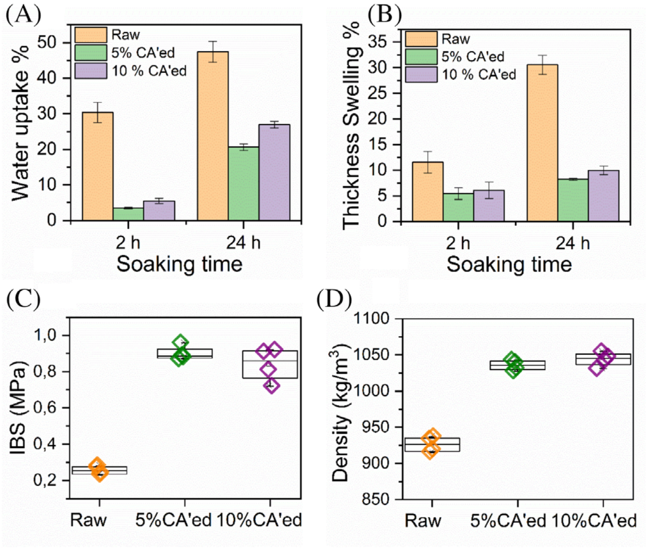

FIGURE 6 The comparison of wood panel (A), 2 and 24 h water absorption (WA) of raw, 5% CA'ed and 10% CA'ed fibers, (B) 2 and 24 h thickness swelling (TS) of raw, 5% CA'ed and 10% CA'ed fibers, (C) density of raw, 5% CA'ed and 10% CA'ed and 100% CA'ed fibers, and (D) internal bond strength (IBS) of panels made of raw, 5% CA'ed and 10% CA'ed fibers.

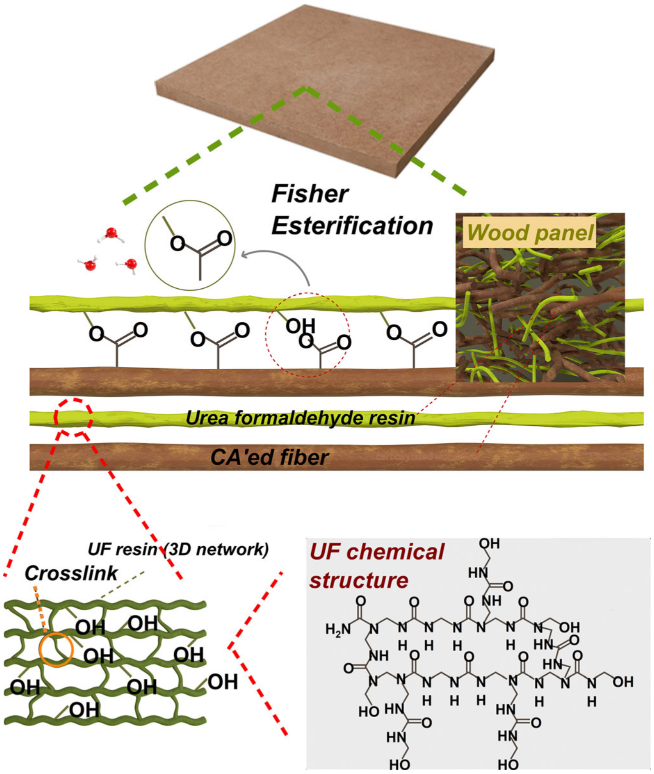

FIGURE 7 The reaction mechanism between UF and modified fibers indicates a crosslinking mechanism in both UF resin and UF resin with carboxylated wood fiber. As a result of this reaction, denser and more compact structures of the panels were obtained, further decreasing water penetration and swelling. Furthermore, it can be attributed to their enhanced interaction with the surrounding urea formaldehyde matrix during the curing process.

point in 2 h. Still, the WA of the panels with modified fibers was reduced by half after 24-h soaking. Therefore, not only do the slow kinetics but also the closure of the pits in the modified fibers play a crucial role. The reduction in the number of open pores or capillary channels in the modified wood fibers limits the pathways through which water molecules can penetrate the fiber structure, thus lowering the overall water uptake.

The effect of modification on the WA is more apparent in a short time, whereas the effect on TS becomes more significant for the TS at long soaking times. The panel with raw fibers shows about 30% swelling, while the swelling remains less than 10% in the modified fiber, suggesting their enhanced dimensional stability.[47] Since the swelling occurs across the panel thickness (opposite to the press direction) by repulsion of the individual wood fibers upon hydration, the reduced TS in the composites with the modified fibers implies an improvement in the internal bonding. The IBS of the panels increased from ≈0.27 MPa in panels with raw fibers to ≈0.89 MPa in panels with 5% modified fibers due to the presence of carboxylic acid groups on the wood surface, leading to stronger interactions with the resin. Increasing the fraction of modified fibers from 5% to 10% caused a slight decrease in IBS (on average) likely due to inhomogeneous mixing with the raw fibers. This also explains the minor deterioration of the WA and TS performance observed for these panels. Nevertheless, ≈ a 3.3-fold increase in IBS (Figure 6C) by incorporating just 5% modified fibers is remarkable. IBS also promotes the densification of the panels (Figure 6D), resulting in a more tightly packed structure due to enhanced interaction with the UF resin.[48,49] The improved density observed in the MDF panels made from modified fibers in Figure 6D can be attributed to several factors. The nitric acid steam treatment introduces carboxylic acid groups onto the fibers, enhancing their hydrophilicity and improving their interaction with the adhesive. This results in better adhesive penetration, stronger bonding, and more efficient fiber alignment during pressing, which reduces void spaces and increases compaction, contributing to higher panel density. Additionally, the chemical modification reduces the fiber diameter, making them thinner and less rigid, which allows for greater compressibility under pressure. This reduces the volume occupied by the fibers due to reduced thickness, leading to denser MDF panels (see Figure S5). Together, these effects improved adhesive interaction, greater compressibility, and more efficient fiber packing.[36,49] Consequently, this denser structure offers more contact points between the fibers and the resin matrix, and effective load transfer between the fibers, thus resulting in greater resistance to deformation and better overall mechanical performance.[48,49]

Additionally, the modified wood panels demonstrate good performance compared with the requirements specified in the EN 622-5:2006 (E) standard[50] for interior-grade particleboards. According to this standard, the IBS should reach a minimum of 0.65 N/mm^2, and the acceptable TS after 24 h is 17%. Our modified fiber panels, however, achieve an IBS close to 1 N/mm^2 and a TS of approximately ∼%8, thus satisfying the standard requirements for enhanced durability and stability in interior applications. Compared to values reported in the literature,[51–53] where panels made solely from pine fibers exhibit higher IBS and a reduction in both swelling and WA. These improvements highlight the effectiveness of our modifications in enhancing panel stability and resistance to moisture.

The physical performance of the composite panels is influenced by the curing behavior of the UF resin. Figure 8 displays the characteristic DSC curves of UF resins, acquired at a heating rate of 10°C/min within the temperature range of 25–200°C. UF resins underwent an exothermic curing reaction attributed to the heat generated from the polycondensation reaction involving the primary amino groups of free urea and the hydroxymethyl groups (—CH$_2$OH).[54] In the presence of raw fibers, the peak temperature of the curing of UF resin was decreased from 165.98 to 147.21°C. The decrease of the curing temperature continues further in the presence of the modified fibers and progressively decreases to 100.67, 89.31, and 75.97°C for 15-min, 30-min, and 60-min treated fibers, respectively (see Table 2). These findings suggest that the initiation of polymerization occurred more rapidly in the UF resin with modified fibers compared with unmodified fibers with two crosslinking mechanisms. One is that acidic pH will accelerate the condensation reaction (crosslinking of —OH groups to form ether bridges in the UF resin). The addition of modified fibers to the UF resin accelerates the curing

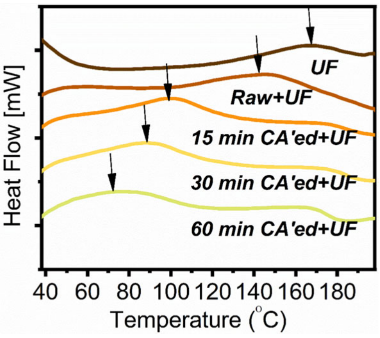

FIGURE 8 Differential scanning calorimetry thermograms of UF resin and its mixtures with unmodified and 15-min, 30-min, and 60-min modified fibers. The arrows show the location of the peak points.

TABLE 2 The comparison of T_{onset}, T_{endset}, and T_{peak} of UF resin and its mixtures with unmodified and 15, 30, and 60 min modified fibers.

	UF only	Raw fiber-UF	15 min modified fiber-UF	30 min modified fiber-UF	60 min modified fiber-UF
T_{onset}	132.84	110.09	63.28	49.89	46.43
T_{endset}	186.35	179.86	127.47	118.23	111.13
T_{peak}	165.98	147.21	100.67	89.31	75.97

initiation. This change can be related to the presence of carboxylic acid groups on the surface of the wood fibers, which can facilitate the crosslinking of the resin molecules due to the pH of the reaction environment. However, excessive acidity can cause the bonds to break down over time due to moisture.[55] This breakdown mainly occurs at the interface between the adhesive and wood fibers, resulting from decomposition, swelling, or shrinking. Consequently, the methylene linkages within the cured resins begin to degrade. This is another reason (apart from the structural breakdown and reopening of the pits) for not using 30-min and 60-min treated fibers in the panel production. Another way of having crosslinking is the reaction between the carboxylic acid groups of the fibers and the —OH groups of the resin to form ester bonds[47,56,57] (see Figure 7). When carboxylated fibers are incorporated into a resin matrix containing hydroxyl-functionalized components, such as UF resins, esterification occurs. This chemical reaction involves the condensation of —COOH and —OH groups to form ester bonds (—COO—), which act as crosslinks within the composite.[58,59] This reaction enhances mechanical strength and composite properties. However, excessive carboxylation leading to excessive acidity, as observed in 60-min treated fibers, results in a significant reduction in the curing onset temperature, as confirmed by DSC analysis.[60–63] This reduction increases the risk of precuring during manufacturing, disrupting the production process. To address the issue of precuring,[63] it is essential to carefully control the modification conditions, particularly the treatment time. Based on DSC analysis, 15-min treated fibers achieved an optimal balance between effective carboxylation and preserving fiber integrity. The partial pit closure observed in these fibers, without surface damage, enhances their interaction with UF resin while maintaining desirable curing conditions. Tests on density, IBS, TS, and WA confirmed that the 15-min treatment provides both enhanced mechanical strength and optimal physical properties in the final product.

Overall, pH influences the kinetics and energetics of the curing reactions in UF resins, impacting the temperature range, reaction rates, and overall efficiency of the curing process. Understanding and controlling the pH of the system is essential for achieving the desired curing characteristics and properties in the final cured resin product.

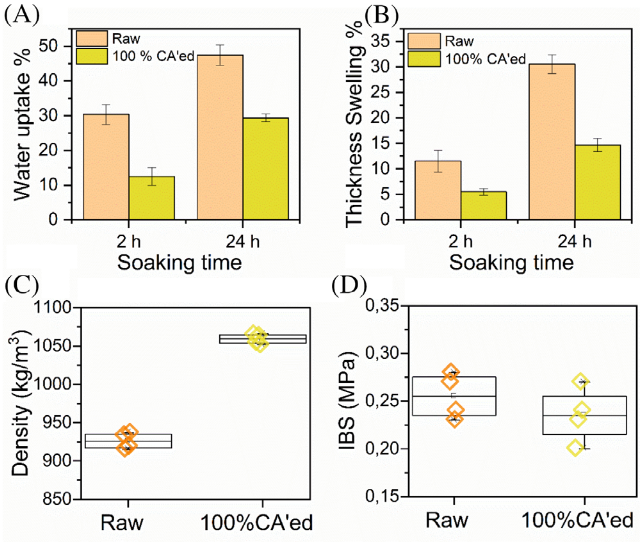

FIGURE 9 The comparison of wood panel (A) 2 and 24 h water absorption (WA) of raw and 100% CA'ed fibers, (B) 2 and 24 h thickness swelling (TS) of raw and 100% CA'ed fibers, (C) density of raw and 100% CA'ed fibers, and (D) internal bond strength (IBS) of raw and 100% CA'ed fibers.

The impact of lower curing temperatures was assessed on the panels fabricated from 100% unmodified and 100% carboxylated fibers (15-min treated) using different curing temperatures. Specifically, the panels made from 100% carboxylated fibers were cured at 150°C (≈50°C higher than their peak temperature) while those from unmodified fibers underwent standard curing at 200°C (also ≈50°C higher than its peak temperature) using the same panel production methods detailed in the materials and methods sections. Despite lower press temperatures, the panels with modified fibers exhibit significantly lower water uptake (Figure 9A), decreased TS (Figure 9B), enhanced density (Figure 9C), and similar IBS values (Figure 9D).

There is an opposite trend between Figures 6 and 9 in terms of IBS and density. This can be explained by the fact that Figure 6 shows samples containing a mixture of unmodified and carboxylated fibers, while Figure 9 presents data for panels made entirely from 100%

carboxylated fibers. The contrasting trends highlight the influence of fiber composition and curing conditions on the IBS and density of the panels. Figure 6 shows a positive correlation between density and IBS, with crosslinking occurring not only between the resin matrix and the fibers but also between unmodified fibers (rich in hydroxyl groups) and carboxylated fibers (rich in carboxylic acid group). This enhanced crosslinking in mixtures leads to higher IBS values and greater density due to the more compact structure formed, improving mechanical strength.[64,65]

In contrast, Figure 9 shows data for panels made entirely from 100% carboxylated fibers, where reduced hydroxyl groups limit crosslinking potential. The crosslinking primarily occurs between carboxylic acid groups on the fibers and the resin matrix, leading to a similar packing structure without significantly changing the density. The reduced curing temperature of 150°C for the 100% carboxylated fibers also impairs the bonding efficiency, leading to lower IBS despite similar density.[46,66] In summary, while the curing temperature and fiber surface chemistry influence the IBS, panels with modified fibers maintain comparable IBS to unmodified fibers, offering improved water resistance and dimensional stability. Furthermore, lowering the curing temperature in panel production without sacrificing the mechanical properties offers advantages in terms of energy consumption needed to heat the manufacturing equipment to the desired temperature as well as to cool the final products. Thus, not only does the catalyst-free modification process itself contribute toward sustainability but also the effects on interaction with the adhesive help minimize greenhouse gas emissions associated with energy production.

In addition to these mechanical and dimensional improvements, the formaldehyde emission results reveal further benefits of the modifications. Panels made from unmodified fibers exhibit a formaldehyde emission of 11.40 ± 0.57 mg/100 g, while panels incorporating 10% CA-ed fibers show a slightly reduced formaldehyde emission of 9.71 ± 0.021 mg/100 g, corresponding to a reduction of approximately 14.82%. The reduction can be explained by the fact that CA modification may introduce functional groups, such as carboxylic groups,[56] which react with free formaldehyde and methylol groups, forming stable bonds due to extra crosslinking[57] and further reducing its release.[47,67] Additionally, the modified panels play a role in restricting the diffusion of formaldehyde gas because a tighter fiber network can reduce free formaldehyde gas by effectively trapping it within the modified structure. These results are consistent with findings from previous investigations into UF resins and particleboard production.[5,68] Typically, using a 1.22 molar ratio UF resin results in panels with formaldehyde emissions within the E2 range (>10 mg/100 g $\sim$ ≤ 30 mg/100 g). Modification with CA fibers resulted in a reduction in formaldehyde emissions, bringing the panels closer to the E1 standard (≤ 10 mg/100 g),[68] while enhancing their mechanical and dimensional stability.

4 | CONCLUSIONS

In conclusion, our investigation into the carboxylic acid formation process through nitric acid gas treatment in a closed system minimizing environmental impact and health risks and then subsequent modification of wood fibers has provided valuable insights into the formation of robust covalent bonds between carboxylic acid-containing wood fibers and UF resin. This highlights the method's potential in enhancing the overall strength of wood fibers, with IBS increasing 3.3-fold (from 0.27 to 0.89 MPa) in panels treated with 5% carboxylated (CA) fibers. Dimensional stability improved significantly, with WA decreasing from 30.38% in untreated panels to 3.46% in treated ones. Additionally, the curing temperature of the adhesive was lowered by 50°C without compromising composite strength, highlighting the practical benefits of this approach. The carboxylation process not only enhances the strength of the fibers but also introduces hydrophilic characteristics, so this provides an improvement in adhesion and also offers a solution to challenges associated with cost and energy consumption. The precision of this novel method in targeting the surface chemistry of wood fibers contributes to improved adhesion and compatibility with synthetic resins. Additionally, the formaldehyde emissions from modified fiber panels (9.71 ± 0.021 mg/100 g) were lower than those from unmodified panels (11.40 ± 0.57 mg/100 g), highlighting the effectiveness of the modification process in reducing emissions and meeting emission standards.

Overall, these modification techniques initiate new ways for further exploration and optimization of carboxylation processes. This approach not only aligns with sustainability goals by potentially reducing environmental impact but also advances the field of wood-polymer interactions, leading to improved performance and new uses for wood-based materials.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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