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Research on Enhancing the Comprehensive Performance of Fir Wood through Chemical Modification with a Biobased Unsaturated Polyester

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ABSTRACT: Fir wood was modified using epoxy soybean oil, diethylene glycol, and maleic anhydride as raw materials to enhance its mechanical properties, thermal stability, and water resistance. Diethylene glycol first opens the epoxy ring of the soybean oil and then reacts with maleic anhydride to produce an esterification reaction. The product modifies the fir wood through a chemical impregnation method. A systematic evaluation of the modified wood's weight gain ratio, density, mechanical properties, thermal stability, water resistance, and microstructural changes was conducted. The results show that the compressive strength increased from 38.1 to 94.9 MPa, the water absorption rate decreased from 158.03 to 6.93%, and the thermal stability was also enhanced. This study provides a simple, low-cost, and green method for improving the comprehensive performance of fast-growing fir wood, offering new insights for achieving sustainable development and green chemical engineering.
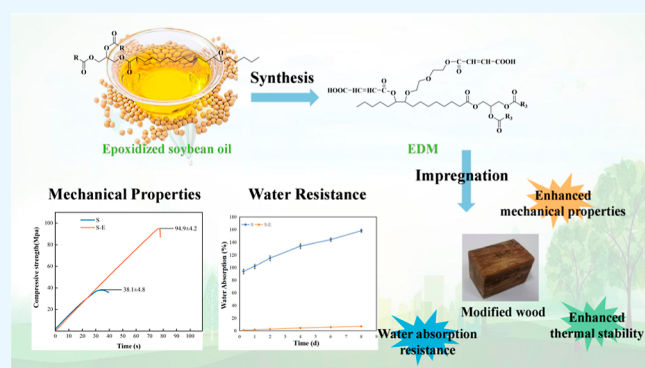
1. INTRODUCTION

Today, wood has become an incredibly important natural and renewable resource due to its ease of processing and high strength. It is widely used in construction, furniture, and decorative items.[1,2] However, natural forests cannot meet the growing demand for wood, and excessive logging can lead to environmental degradation. As a result, artificially cultivated fast-growing wood has caught public attention due to its rapid growth rate, high yield, and short harvesting period, making it an important alternative to natural wood.[3,4] Fast-growing wood can meet the market's increasing demand and is one of the methods to practice sustainable development and protect nature, attracting widespread attention from scholars today.[5,6]

The modification of fast-growing wood is necessary. Although it has the advantages of high yield and rapid growth, its lower wood strength and susceptibility to corrosion significantly limit its application scope.[7−10] Chemical modification is an effective method to improve the mechanical properties, dimensional stability, flame retardancy, and corrosion resistance of fast-growing wood. Among various chemical modification techniques, resin impregnation is considered to be an efficient, low-cost, and simple treatment method that significantly enhances the wood's multifaceted properties.[11,12] The most common chemical modification methods include thermosetting resin treatment,[13] acetylation,[14] and furfurylation,[15] among others. Recently, Peng[16] and

colleagues have modified fast-growing poplar wood using 1,3-dihydroxymethyl-4,5-dihydroxyethylurea (DM) and alkaline lignin through wood impregnation, effectively improving the wood's dimensional stability, mechanical properties, and corrosion resistance.

Biomaterials are characterized by their wide availability, low cost, high quantity of functional groups, and high reactivity. A current hot research topic is the production of wood−plastic composites using biomass raw materials such as plant oil polyols, glycerol, maleic anhydride, and lignin. Milena et al.[17] produced polyurethane (RPUF) through the cyclization of rapeseed oil and its reaction with diols, which exhibited good mechanical and biological performance, high-dimensional stability, high aging resistance, and low water absorption rate, but their experiment applied polyester in the pumice applications of the cosmetics industry. Maleic anhydride, a common anhydride, is usually prepared from furfural. Furfural can be extracted from various agricultural products, such as corn cobs, wheat bran, and sawdust.[18] Therefore, maleic

anhydride is a derivative of biomass materials. It is characterized by its strong acidity, low melting point, and the presence of a high content of carboxyl and unsaturated bonds after ring opening. Maleic anhydride, when in contact with hydroxyl-containing compounds at an appropriate temperature, will open its ring and undergo esterification with hydroxyl groups.[19]

However, there are few published studies that apply biobased unsaturated polyester resin (UPR) to wood reinforcement and modification. For example, Costa et al.[20] studied a novel UPR based on soybean oil and coconut oil, which has high thermal stability. Das et al.[21] prepared a novel UPR from tung oil, which has higher impact strength, creep resistance, modulus, and hardness. Hence, it is necessary to develop a new method to prepare a biobased unsaturated polyester on the basis of RPUF and apply it to the performance modification of fast-growing wood.

This paper focuses on the preparation of the unsaturated polyester EDM by opening the ring of epoxy soybean oil with diethylene glycol and reacting it with maleic anhydride. A biobased wood-plastic composite material is produced using a chemical impregnation method (Figure 1). This study aims to broaden the application of vegetable oil-based unsaturated polyester in the modification of fast-growing wood, promote a harmless and low-cost method for modifying fast-growing wood, and provide an environmentally friendly and green approach for the production of biobased unsaturated polyester.

2. EXPERIMENTAL SECTION

2.1. Main Raw Materials and Instruments. *2.1.1. Experimental Materials and Reagents.* Epoxy soybean oil and fir wood were purchased from the market; diethylene glycol (DEG, A.R.) was acquired from Tianjin Balloon Chemical Reagents Science & Technology Co., Ltd.; *p*-toluenesulfonic acid (A.R.) was obtained from Xilong Scientific Co., Ltd.; maleic anhydride (MA, A.R.) was sourced from Shanghai Reagent Factory no. 3; benzoyl peroxide (BPO, A.R.) was procured from Sinopharm Chemical Reagent Co., Ltd.; hydroquinone (HQ, A.R.) was provided by Sinopharm Chemical Reagent Co., Ltd.; styrene (St, A.R.) was produced by Shanghai Aladdin Bio-Chem Technology Co., Ltd.; and divinylbenzene (DVB, A.R.) was purchased from Tianjin Chemical Reagents Company.

2.1.2. Analytical and Testing Instruments. The instruments used are as follows: rotary viscometer: NDJ-1 model, Shanghai Precision & Scientific Instrument Co., Ltd.; Fourier transform infrared (FTIR) spectrometer: Spectrum Two, PerkinElmer, USA; compression testing machine: YAW-100D, Jinan Zhonglu Chang Experimental Machine Manufacturing Co., Ltd.; thermogravimetric analyzer: TGA-50, Shimadzu Corporation, Japan; X-ray photoelectron spectrometer: PHI5000 VersaProbe-II, Ulvac-Phi, Japan; scanning electron microscope: TESCAN VEGA 3, TESCAN, Czech Republic; nuclear magnetic resonance hydrogen (^{1}H NMR) spectrum: AV III HD 400 MHz, Bruker, Germany.

2.2. Preparation of Modified Wood Samples. *2.2.1. Synthesis of the Castor Oil-Based Unsaturated Polyester.* Epoxy soybean oil and diethylene glycol were mixed in a 1:1.5 molar ratio with 0.9 wt % *p*-toluenesulfonic acid added to a three-necked flask. The mixture was stirred and heated to 140 °C. After maintaining the temperature for 4 h, the epoxy value of the product was measured according to GB/T 1677−1981.[22] Once the epoxy value dropped to zero, the
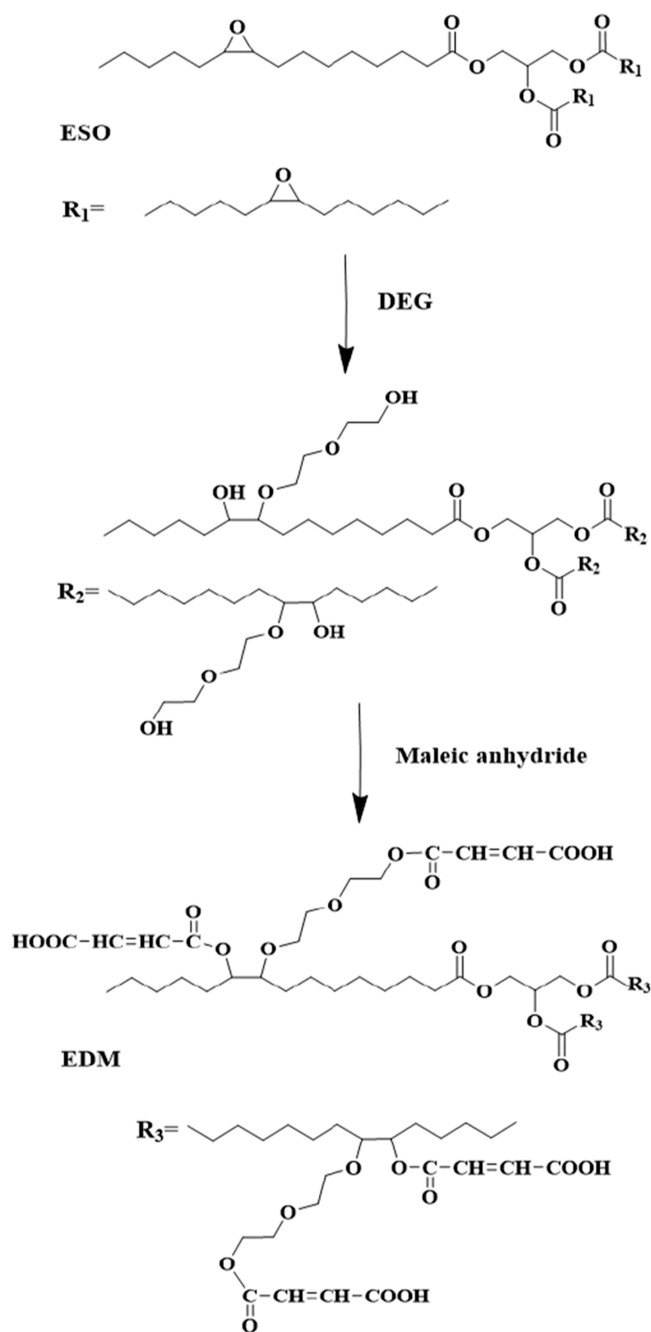

Figure 1. Schematic diagram of the synthesis of the unsaturated polyester EDM.

mixture was cooled to 70 °C, and maleic anhydride was added in an amount equal to the molar number of hydroxyl groups in the system. The mixture was stirred for 30 min to ensure thorough mixing, then 1 wt % *N*,*N*-dimethylbenzylamine and 0.02 wt % hydroquinone were added, and the temperature was raised to 90 °C. After reacting for 4 h, the product, EDM, a reddish-brown substance, was prepared.

2.2.2. Modification of Wood Samples. To ensure consistency among the fir wood specimens (cut along the grain of the wood to obtain wooden blocks with dimensions of 20 × 20 × 30 mm), they must be hewn from an undamaged, uniform board with a density approximately at the mean value (0.36 ± 0.03 g/cm³). Initially, the specimens underwent vacuum dehydration at 103 ± 2 °C for a duration of 2 h.

Subsequently, they were placed in a container designed for impregnation. The samples were subjected to a prevacuum of −0.08 MPa for 2 h, which preceded the introduction of the EDM impregnating solution. This was followed by a 2 h atmospheric pressure immersion to guarantee thorough permeation. Finally, the wood pieces were heat-treated at 100 °C for 2 h to finalize the modification process.

2.3. Test and Analysis Methods. *2.3.1. Determination of Gel Content in the Impregnation System.* The gel content of the EDM impregnation system was determined according to the method described in GB/T 2576−2005.[23] The soluble components in the cured UPR impregnation system were extracted using a Soxhlet extractor with ethyl acetate at a temperature close to its boiling point. The insoluble components were considered as the degree of curing of the resin, α, and calculated using eq 1

$$\alpha = \frac{m'}{m} \times 100\%$$

(1)

- m is the mass of the sample before extraction, in mg;
- m' is the mass of the sample after extraction, in mg.

The degree of curing (β) of the UPR impregnation system in wood: The degree of curing of the UPR impregnation system within the wood was determined by referring to the method for determining the degree of curing of the UPR impregnation system and calculated using eq 2 to find the curing degree (β) of the UPR impregnation regime within the wood.

$$\beta = \frac{m_3 - m_2(1 - c_0)}{m_1 - m_2} \times 100\%$$

(2)

- m_1 is the mass of the modified wood sample before extraction, in mg;
- m_2 is the mass of the original wood in the modified wood sample before extraction, in mg;
- m_3 is the mass of the modified wood sample after extraction, in mg;
- c_0 is the logarithmic mass loss rate after extraction, in percent, with five samples selected.

2.3.2. Determination of Impregnation Rate and Curing Weight Gain Rate of Modified Wood. The impregnation rate (IY) of wood with the EDM impregnation system is calculated using Formula 3, and the weight gain rate upon curing (WPG) is calculated using Formula 4

$$IY = \frac{W_2 - W_1}{W_1} \times 100\%$$

(3)

$$WPG = \frac{W_3 - W_1}{W_1} \times 100\%$$

(4)

W_1 is the mass of the log sample, in grams; W_2 is the mass of the wood sample after impregnation, in grams; and W_3 is the mass of the wood sample after curing, in grams. Five samples were selected.

2.3.3. Determination of Water Absorption of Modified Wood. According to the measurement method in GB/T 1934.1−2009,[24] with a measurement period of 7 days, the water absorption rate (A) of the modified wood samples is calculated using the following formula

$$A = \frac{m_n - m_0}{m_0} \times 100\%$$

(5)

- where m_0 is the mass of the wood sample when completely dry, in grams;
- m_n is the mass of the wood sample after water absorption, in grams.

The water resistance efficiency of the modified wood samples is calculated using Formula 6

$$WRE = \frac{A_0 - A}{A_0} \times 100\%$$

(6)

- where A_0 is the water absorption rate of the log sample, in percent;
- A is the water absorption rate of the modified wood sample, in percent.
- Five samples were selected.

2.3.4. Determination of Compressive Strength along the Grain of Modified Wood. In accordance with the method specified in GB/T 1935−2009,[25] the compressive strength along the grain of wood samples is measured using a compression testing machine. The sample is placed in the center of the spherical movable support of the testing machine in the direction of the grain, the loading speed is set to 0.5 KN/s, and the load at failure is recorded. The compressive strength (σ), in MPa, of the modified wood sample along the grain is calculated using Formula 7

$$\sigma = \frac{P_{max}}{b \times t}$$

(7)

In the formula, P_{max} is the load at failure, in Newtons (N); b is the width of the sample, in millimeters (mm); and t is the length of the sample, in millimeters (mm).

2.3.5. Determination of Wood Density and Profile Density of Modified Wood. The densities of the original wood (ρ_{log}) and modified wood (ρ_m) are determined using the method specified in GB/T 1933−2009.[26] The profile density of modified wood (ρ_s) is determined using the pycnometer method as described in GB/T 15223−2008[27] and calculated using Formula 8, in g/cm³. In the formula, m_0 is the mass of the pycnometer filled with distilled water, in grams (g); $m1$ is the mass of the modified wood sample, in grams (g); m_2 is the total mass of the pycnometer filled with distilled water with the modified wood sample inside, in grams (g); and ρ_{water} is the density of distilled water, in g/cm³.

$$\rho_s = \frac{m_1}{m_0 + m_1 - m_2}\rho_{water}$$

(8)

2.3.6. Infrared Spectroscopy Analysis. FTIR spectroscopy was utilized to characterize the hydrolysis products of castor oil, the esterification products, and the modified wood samples. Attenuated total reflection detection was employed, with the number of reflections set to 8. The test wavenumber range covered 4000−400 cm^{-1}.

2.3.7. ^1H NMR Spectrum. Deuterated acetone was used as the solvent, and the magnetic field was set to 400 M for analyzing epoxy soybean oil and its ring-opening and esterification products with a Bruker Avance 400 NMR spectrometer.

2.3.8. Scanning Electron Microscopy. Original and modified wood samples were cut into tangential cross-section samples measuring 5 × 5 × 2 mm and examined under a scanning electron microscope to study their surface microstructure. To avoid charge accumulation during characterization, the samples were sputter-coated with gold, and tests

were conducted at magnifications of 1000 and 5000× under an accelerating voltage of 20 kV.

2.3.9. X-ray Photoelectron Spectroscopy. Original and modified wood samples were cut into tangential cross sections measuring 5 × 5 × 2 mm, and their surface chemical elements were analyzed using X-ray photoelectron spectroscopy (XPS). An Al anode was used as the X-ray source, with a power of 50 KW, a pass energy of 46.95 eV, and step sizes of 0.8 eV for the full spectrum and 0.2 eV for the high-resolution spectrum. The binding energy for aliphatic carbon's C 1s (284.8 eV) was used for charge correction.

2.3.10. Thermogravimetric Analysis. The specimens were ground into powder with a maximum particle size of 0.2 mm. Thermogravimetric analysis (TGA) was then utilized to evaluate the thermal stability of the altered wood material. During the analysis, a nitrogen atmosphere was maintained at a flow rate of 20 mL/min, and the temperature of the specimens was incrementally increased from ambient temperature to 800 °C at a rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. Study on the Curing Conditions of EDM. To explore the optimal curing conditions and material ratios for EDM, this study conducted a single-round $L_9(3^4)$ orthogonal experiment, diluting with styrene in a 3:1 mass ratio. The factors examined included the amount of cross-linking agent, initiator quantity, curing temperature, and curing time, with the gel content of the cured product as the reference. The results showed that the curing temperature and time significantly affect the resin's curing outcome.

The optimal conditions selected from the orthogonal experiment yielded a gel content of 89.8%. It was found that although the synthesized UPR oligomer contained other components, they had little effect on the curing of EDM. This is attributed to the complex curing process of unsaturated polyester (UPR), where the C=C bonds on the linear unsaturated polyester molecular chains undergo free radical copolymerization with styrene, forming four types of cross-linked structures: (I) intermolecular cross-linking aided by styrene; (II) intramolecular cross-linking aided by styrene; (III) polyester molecular branching with the help of styrene; and (IV) homopolymerization of styrene.[28] Moreover, the steric hindrance effect results in some unreacted unsaturated double bonds within the curing cross-linked network of the unsaturated polyester, making the network more disordered. Thus, other components in the UPR oligomer can also facilitate further curing of EDM.

3.2. FTIR Analysis of the Various Stages of the Biobased Unsaturated Polyester EDM. Characteristic bands of epoxy soybean oil, its ring-opened product, and the synthesized resin are shown in Figure 2. The epoxy ethane ring stretching vibration band at 823 cm^{-1} and the C−O stretching vibration band at 1156 cm^{-1} indicate the presence of epoxy groups.[29,30] The C=O stretching vibration band near 1750 cm^{-1} indicates the presence of ester groups; the −CH stretching vibration band near 2900 cm^{-1} indicates the presence of alkyl groups. The broad and strong −OH stretching vibration band near 3450 cm^{-1}, along with the C=O stretching vibration band near 1750 cm^{-1}, suggests the presence of carboxyl groups, and the broad and strong −OH stretching vibration band near 3450 cm^{-1}, along with the C−O stretching vibration band at 1156 cm^{-1}, indicates the presence of polyols.[31] In the FTIR spectrum of ED, the characteristic
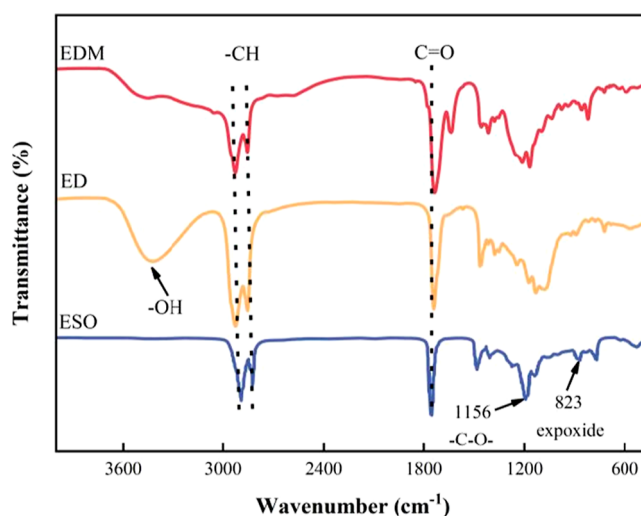

Figure 2. Infrared spectra of the EDM raw material and products at various synthetic stages. In the figure, ESO represents epoxy soybean oil and ED represents the ring-opened product.

band of epoxy ethane at 823 cm^{-1} disappears, and combined with the determination of the epoxy value, it suggests that ESO and DEG have undergone a ring-opening reaction. The absorption bands of alkyl C−H and ester C=O from epoxy soybean oil appear at the same positions in EDM, indicating that the introduction of unsaturated anhydride provides conditions for the cross-linking and curing of EDM.

3.3. ^{1}H NMR Analysis of Products at Different Stages of EDM. The resonance at 0.88 ppm is identified with the end methyl protons of the fatty acid's chain, while the signals between 1.30 and 1.33 ppm correspond to the methylene groups inside the fatty acid chain.[32] The resonance found between 2.80 and 3.10 ppm in Figure 3 is linked to the presence of epoxy groups.[33] The signals at 3.62, 3.72, 3.82, and 4.37 ppm are related to the methylene groups of the DEG component, and a peak at 3.56 ppm verifies the hydroxyl end groups in the product's structure,[33] indicating the successful opening of the epoxy soybean oil ring by DEG. Additionally, the resonances between 6.33 and 6.48 ppm in Figure 3 are attributed to the main chain signals (−CH2=CH−) of maleic anhydride,[34,35] implying that maleic anhydride has reacted through esterification with the ring-opened derivative of epoxy soybean oil.

3.4. Enhanced Modification of Wood. *3.4.1. Basic Performance Analysis of Modified Wood.* The impact of EDM impregnation on fast-growing wood, enhancing its performance, is mainly reflected in impregnation rate, weight gain rate, and water absorption (Table 1).

After impregnation with EDM, the impregnation rate and weight gain rate of fir wood both exceeded 200%. The density differences across the outer, middle, and inner cross sections of the modified fast-growing wood were minimal, showing an increase over the original wood's density and exhibiting a gradual decrease from the exterior toward the interior. This suggests that the resin effectively penetrated the wood's interior, with the impregnation impact diminishing from the outer to the inner layers. The EDM impregnation system's lower viscosity allowed for better filling of the wood's internal voids, thereby enhancing the modification effect and rendering it more apt for industrial usage.
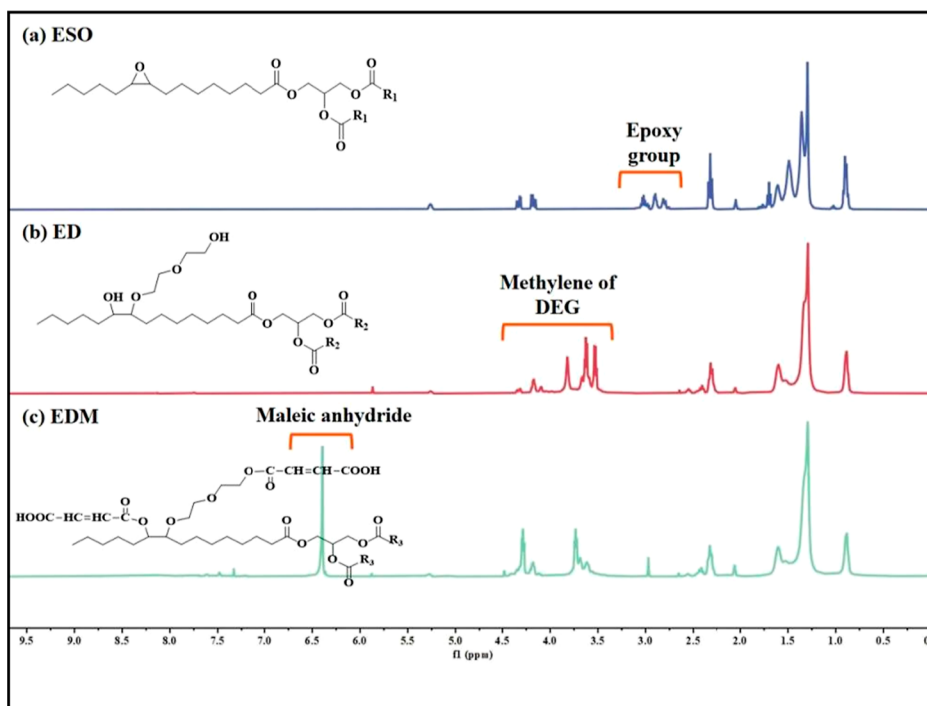
Figure 3. ^{1}HNMR analysis of products at various stages of EDM.

Table 1. Performance Table of Fast-Growing Wood Modified by the EDM Impregnation System[a]

UPR impregnation system	viscosity (Pa·s)	wood type	ρ_{log}(g/cm³)	ρ_m(g/cm³)	ρ_s			IY(%)	WPG(%)
					outer	middle	inner		
EDM	1.24 ± 0.05	S	0.40 ± 0.02	1.02 ± 0.08	1.05 ± 0.07	1.01 ± 0.04	0.97 ± 0.02	219.74 ± 10.26	216.15 ± 9.18

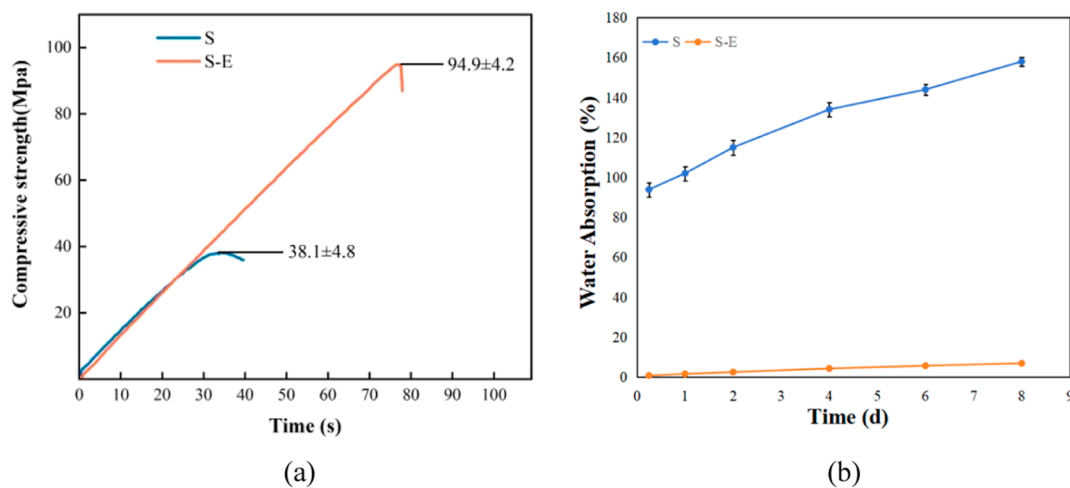[a]In the table, wood type S represents fir wood.

Figure 4. (a) Compressive strength−time curve of modified fir; (b) water absorption rate−time curve of modified fir. In these figures, S-E represents modified fir wood.

The application and hardening of EDM within the wood also resulted in enhanced water resistance and mechanical strengths. Water absorption tests revealed that the water absorption rate of untreated spruce stabilized at 158.03 ± 2.17%, whereas that of the EDM-modified fir dropped to below 20% (Figure 4b). Furthermore, the compressive strength of the modified fir saw an increase from 38.1 ± 4.8 to 94.9 ± 4.2 MPa (Figure 4a).

3.4.2. XPS Analysis of Modified Fast-Growing Wood. The XPS full scan spectra (Figure 5) reveal significant absorption peaks between 283 and 290 and at 532 eV, highlighting that both untreated and treated fir wood surfaces are rich in carbon (C) and oxygen (O) elements. The carbon atoms in wood are
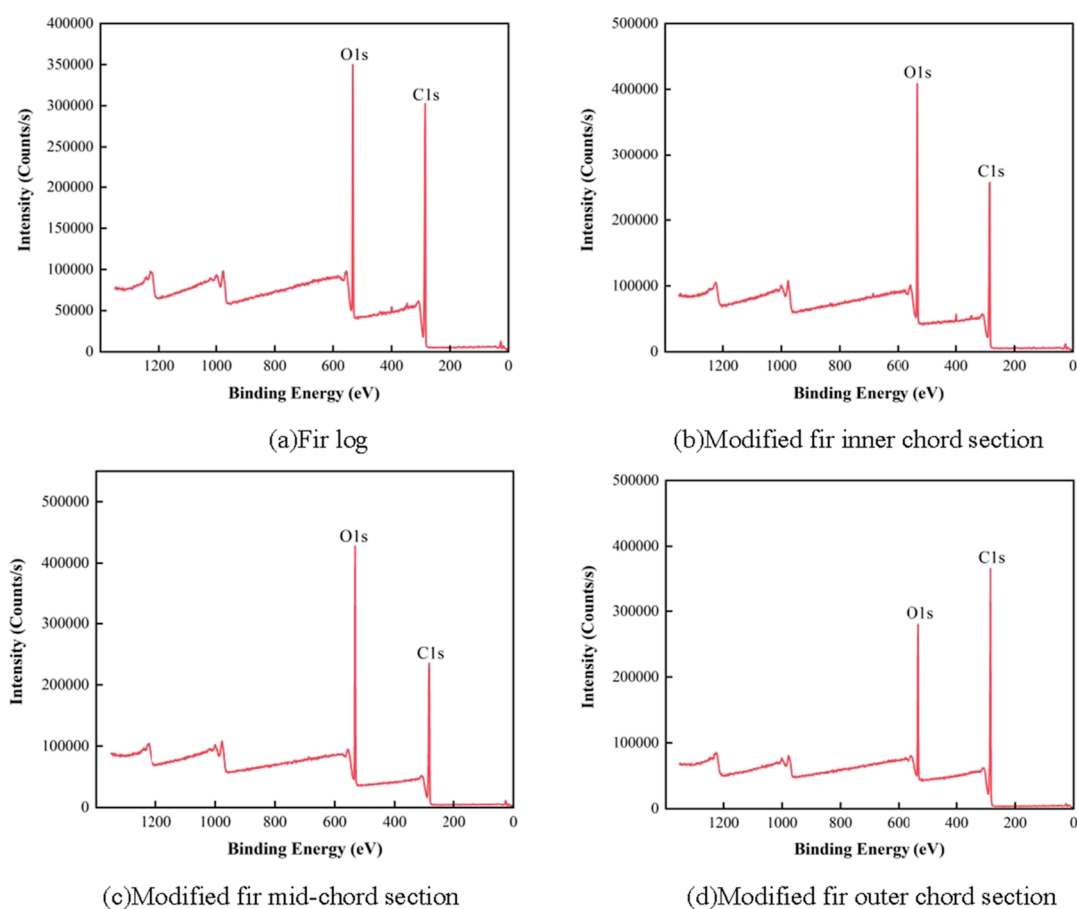
(a)Fir log

(b)Modified fir inner chord section

(c)Modified fir mid-chord section

(d)Modified fir outer chord section

Figure 5. XPS full spectra of fir wood original and modified samples.

categorized into four distinct forms.[36,37] Specifically, in the high-resolution C 1s spectrum (Figure 6), the C1 component is linked to carbon atoms found in aliphatic and aromatic carbon chains, interacting solely with carbon or hydrogen atoms, and exhibits a binding energy of approximately 284.8 eV. This is primarily indicative of the lignin, characterized by a phenylpropane structure within the original wood and the main chain structure of UPR. The C2 and C3 components are associated with C−O structures, representing carbon atoms bonded to two noncarbonyl oxygen atoms or one carbonyl oxygen atom, with binding energies around 286.4 and 288 eV, respectively. These states signify the cellulose and hemicellulose structures in wood, both of which comprise numerous carbon atoms linked to hydroxyl groups.[38] Lastly, the C4 component, with a binding energy of about 289 eV, relates to carbon atoms connected to one noncarbonyl oxygen atom and one carbonyl oxygen atom. This component is in a higher oxidation state, causing a significant chemical shift, and primarily represents the fatty acids and ester groups present in wood extracts and unsaturated polyester resins.

In the table, the density of the original fir wood tangential section is the density of the original wood, while the others represent their respective profile densities.

Table 2 outlines the shifts in the relative amounts of different carbon forms within the inner, middle, and outer tangential sections of both the untreated and treated fast-growing wood samples. A notable increase in the relative content of the C4 component is observed, paralleled by a decrease in the C3 component, a trend that aligns with the density data of the profile. Concurrently, there is an overall rise

in both the oxygen content and the O/C ratio within the treated fast-growing wood samples. This trend suggests that the biobased unsaturated polyester, EDM, has effectively been absorbed into the fir wood. The findings imply that the EDM impregnation process predominantly operates through lateral infiltration, with the impregnation depth diminishing from the outer layers toward the inner layers.

3.4.3. SEM Analysis of Modified Fast-Growing Wood. Scanning electron microscopy (SEM) images showcasing the tangential cross sections of the interior surfaces of both untreated and treated fir wood are presented in Figure 7. The image of the untreated wood's cross-section reveals clear passages without any noticeable residues in the conduits, wood fibers, and ray cell cavities, with the pits remaining open. This demonstrates EDM's capability to infiltrate the wood's interior, facilitating its modification. In contrast, the cross-section of the treated wood shows that the conduits, ray cell cavities, and wood fibers are encapsulated and bonded by resin, with the pits also being filled by resin. The control images, Figure 7e,f, distinctly illustrate the resin's impregnation and curing process within the wood's pits, affirming EDM's effective penetration and interaction with the wood's minor components, all while preserving the wood's microstructure integrity.

Pit channels act as conduits, allowing the entry and movement of small molecules like water between various microstructural cells within the wood. By filling the majority of these internal pits, the EDM resin acts as a barrier against the ingress of water and other small molecules, significantly bolstering the wood's resistance to water. Furthermore, the resin that fills the wood's structure engages in reactions, cross-
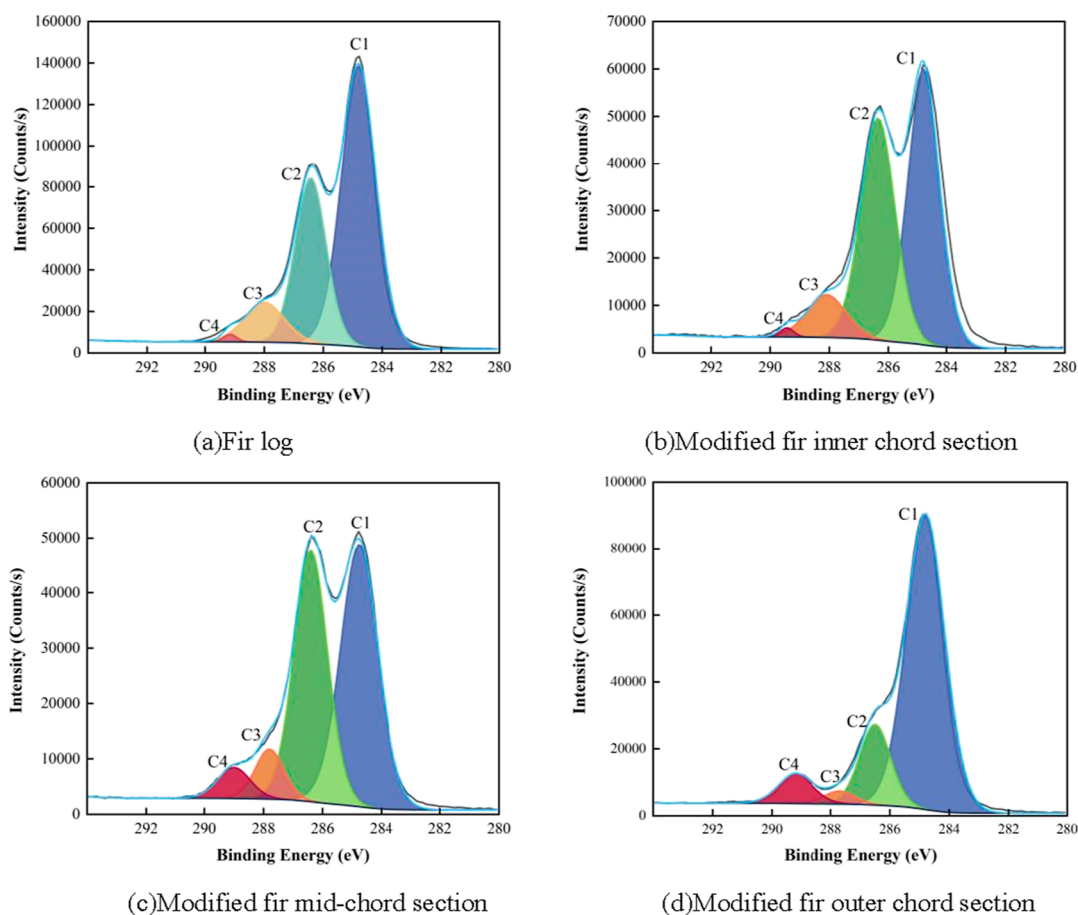
(a)Fir log

(b)Modified fir inner chord section

(c)Modified fir mid-chord section

(d)Modified fir outer chord section

Figure 6. Fine spectra of C 1s of fir logs and modified fir samples.

Table 2. Surface Chemical Element Content of Fir Wood Original and Modified Samples

sample serial number	C(%)	C1(%)	C2(%)	C3(%)	C4(%)	O(%)	O/C(%)	$\rho(g/cm^3)$
fir log chord section	68.44	59.04	30.74	9.63	0.59	31.56	46.11	0.40 ± 0.02
modified fir inner chord section	70.82	54.19	36.72	8.48	0.6	20.83	29.41	0.97 ± 0.02
modified fir midchord section	68.70	49.06	39.50	6.71	4.74	31.30	45.56	1.01 ± 0.04
modified fir outer chord section	79.17	73.30	18.20	1.81	6.69	29.18	36.85	1.05 ± 0.07

linking, or forms hydrogen bonds with the hydroxyl groups present in the wood cells, which contributes to the enhancement of the wood's compressive strength.[39]

The diagram in Figure 8 delineates the process of impregnation and curing of EDM components within the wood's structure. The wood's intercellular spaces and pit channels are identified as the main routes for the penetration of substances into the wood cells. Utilizing vacuum and pressure techniques enables the infusion of EDM, which contains carboxyl and hydroxyl groups, as well as DVB that is characterized by its double bonds, deep into the wood's structure. When heated to a specific temperature, EDM undergoes cross-linking through its double bonds. Concurrently, some of the carboxyl groups may react with the hydroxyl groups present in the wood, and hydroxyl groups from both EDM and the wood may form hydrogen bonds. This process, as highlighted not only in our findings but also in studies by other researchers,[36,37,40,41] results in the EDM resin network being securely anchored within the wood, which is anticipated to significantly enhance wood modification. This method of chemical impregnation was selected for wood modification in our study due to its efficacy.

3.4.4. TGA of Modified Fast-Growing Wood. The TG and derivative thermogravimetry (DTG) spectra depicted in Figure 9, alongside specific data points such as $T_{10\%}$ (the temperature at which there's a 10% mass loss), $T_{50\%}$ (the temperature at which a 50% mass loss occurs), and T_{max} (the temperature of maximum decomposition rate), facilitate the evaluation of the thermal stability of wood samples. Initially, the untreated wood exhibits minor weight loss from room temperature to 100 °C, predominantly due to moisture evaporation from the wood's cell walls. Following this, the thermal breakdown of wood constituents starts, with hemicellulose being the least thermally stable, decomposing first within the 210−300 °C range. A notable mass reduction is observed around 360 °C on the DTG curve, chiefly attributed to cellulose breakdown, while lignin undergoes decomposition across a broader spectrum, from 300 °C up to 500 °C.[42] As temperatures escalate further, decomposition of C−C and C−O bonds occurs, leading to the formation of small molecules like H_2O, CO_2, and hydrocarbons. By 800 °C, the wood's components have fully decomposed, leaving a char residue of approximately 17.33% in fir wood. The DTG curve also reveals that the peak associated with moisture evaporation in treated wood is substantially
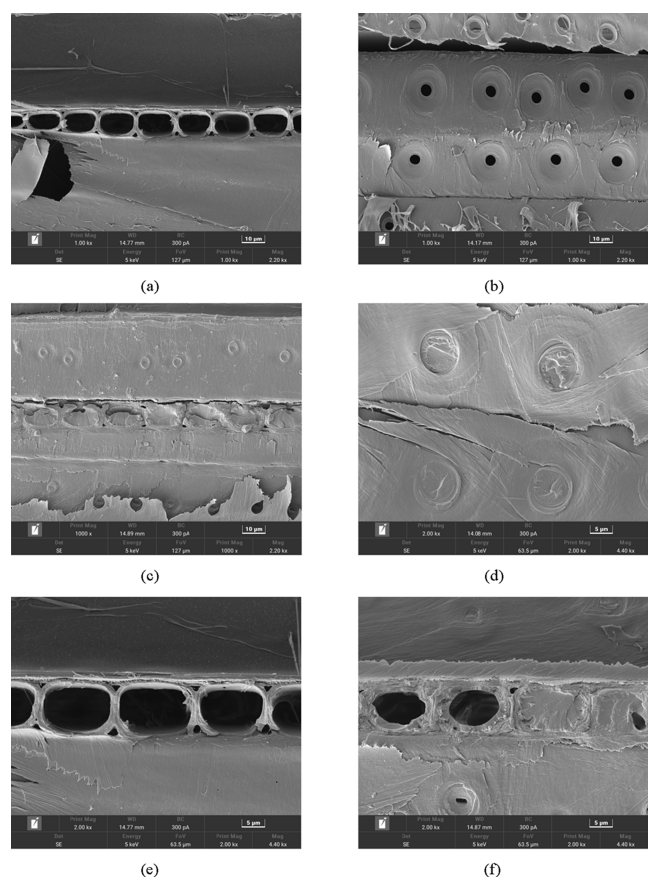
Figure 7. SEM images of fir wood and modified fir wood samples: images (a,b) are SEM images of the tangential section of fir wood, images (c,d) are SEM images of the tangential section of modified fir wood, and images (e,f) are for the control group. Images (a,c) are magnified 1000 times and images (d−f) are magnified 5000 times.

reduced compared to that of untreated wood, indicating that the cross-linked UPR significantly diminishes the wood's ability to absorb water.

Additionally, Table 3 indicates that the protective impact of unsaturated polyester on wood at $T_{10\%}$ is relatively minor. In the 210 to 300 °C range, not only does hemicellulose decomposition occur in the treated wood but also a minor breakdown of UPR. The interval from 300 to 500 °C is

characterized by the thermal decomposition of cellulose, lignin, and any remaining UPR, with the $T_{50\%}$ and T_{max} values for treated wood being marginally elevated by about 10 °C compared to those of untreated samples.[43] This minor increase suggests that the cured UPR offers protection that delays the thermal degradation of wood components. Thus, it is deduced that the infusion and curing of EDM within the wood structure notably enhance the wood's thermal stability.

The thermal decomposition of cured EDM resin can be explained in three main steps. Initial decomposition is observed before 220 °C, where approximately 6 wt % weight loss is due to the evaporation of moisture and uncured materials from the resin surface.[44] Then, a sharp weight loss is observed between 260 and 410 °C, with the DTG peak maximum at 405.25 °C. This is mainly due to the rapid decomposition and volatilization of cured UPR at high temperatures, until the TGA and DTG curves return to their original baseline. Above 500 °C, a gradual weight reduction is observed as the thermally stable char produced during the decomposition process slowly oxidizes. From Table 3, it can also be seen that the cured EDM resin has higher $T_{10\%}$, $T_{50\%}$, and T_{max} stages than both the original and modified wood, indicating that the cured EDM resin itself possesses good thermal stability performance.

In the table, S-E represents modified fir wood and EDM_c represents the cured EDM resin.

4. CONCLUSIONS

This study synthesized a biobased unsaturated polyester (EDM) using epoxy soybean oil, diethylene glycol, and maleic anhydride and modified fir wood through a chemical impregnation method, enhancing the wood's water resistance, compressive strength, and thermal stability. The results indicate that EDM can not only penetrate into the wood's microstructure but also react with the wood, forming a stable cross-linked network within. Compared to the original wood, the modified fir wood's density increased from 0.40 g/cm^3 to 1.02 g/cm^3, its compressive strength increased from 38.1 to 94.9 MPa, its water absorption rate decreased from 158.03 to 6.93%, and its thermal stability was also improved. This experiment organically combines biobased unsaturated polyester with fast-growing wood. It aims to broaden the application scope of fast-growing wood and promote a harmless, low-cost modification method. Additionally, it
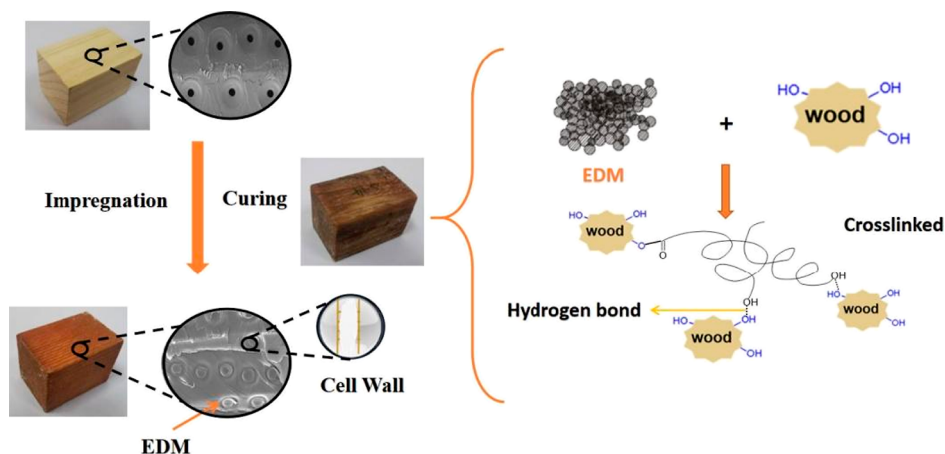

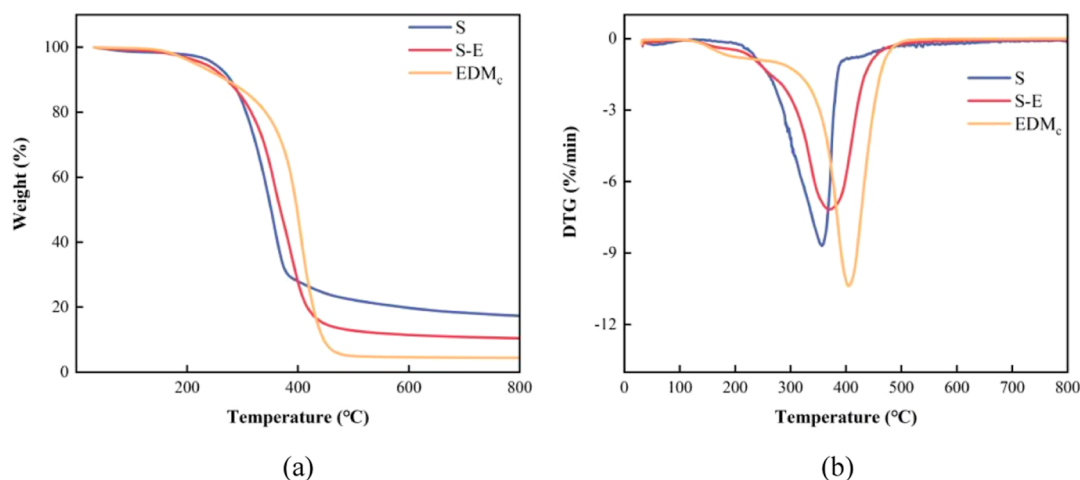**Figure 8.** Schematic diagram of the impregnation and curing reaction of the EDM system inside wood.

Figure 9. TG (a) and DTG (b) spectra of fir wood and its modified wood.

Table 3. TGA Data for Original and Modified Wood Samples

sample	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	residue mass at 800 °C (%)
S	274.87	350.87	356.87	17.33
S-E	279.08	368.08	370.08	10.42
EDM$_c$	278.25	398.25	405.25	4.41

provides an environmentally friendly, green new pathway for the production of unsaturated polyester, aligning with the principles of "green chemical engineering" and sustainable development.

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Notes

The authors declare no competing financial interest.

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