

Comprehensive Characterization of Lignocellulose in Azelaic Acid-impregnated Wood

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Azelaic acid (AZA) impregnation is an effective method for improving the dimensional stability of wood; however, the related microstructural and mechanical changes in lignocellulose remain unclear. In this study, the microstructure and deformation behavior of AZA-esterified wood were investigated using an integrated approach combining thermal analysis, attenuated total reflection infrared (ATR-IR) spectroscopy, wide-angle X-ray diffraction (XRD), and compression testing. When heated below the melting point of AZA, unreacted AZA was observed on the wood surface and within the lumen. In contrast, heating above the melting point promoted diffusion of AZA into the cell wall and induced esterification, which progressed with increasing temperature. The maximum ester content was 1.08 mmol/g dry wood. Heat treatment at 120 °C or higher suggested the formation of cross-links between molecular chains. The relationship between nominal compressive stress (σ) and compression ratio (C) exhibited an inflection point at approximately 10 MPa, suggesting sliding behavior in the intercellular layer under low compressive loads. Furthermore, esterification-dependent differences in cellulose-derived molecular mobility and thermal decomposition behavior were observed.

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INTRODUCTION

Esterification has been used for a long time to plasticize wood. Esterified wood contains hydroxyl groups that are converted to esters, imparting plasticity even in the dry state. Various esterifiers, including fatty acid chlorides (Shiraishi *et al.* 1979a, 1982) and fatty acids, have been investigated in the presence of trifluoroacetic anhydride (Arni *et al.* 1961; Nakano and Nakamura 1986). Esterifiers must contain at least six carbon atoms to enhance the thermoplastic properties of wood (Shiraishi *et al.* 1979b), although this requirement decreases as the carbon chain of the grafted radical lengthens (Shiraishi *et al.* 1982). The free volume generated by the loss of hydrogen bonds during esterification is believed to increase the flexibility of molecular chains, thereby facilitating fusion (Nakano 1994). Solvent-free esterification has also been explored (Thiebaud and Borredon 1995; Thiebaud *et al.* 1997), as has esterification using vinyl esters (Jebrane and Sèbe 2008). Recently, methods for rapid or room-temperature esterification of wood have been reported (Abe *et al.* 2020, 2021). Although these approaches have been demonstrated at the laboratory scale, few are commercially viable because of the need for a controlled environment to ensure safety. Moreover, it is challenging to impregnate wood cell walls

with many organic solvents (Ishimaru and Murata 1996), making pressurizers and other equipment essential for efficient delivery of the desired substances into the cell walls.

This study focused on esterification using azelaic acid (AzA), a naturally derived dicarboxylic acid. Itoh reported that when wood was impregnated with AzA and heated above its melting point, the rate of weight gain decreased, but bulking increased (Itoh 1983). Bulking reflects wood swelling due to the solute and indicates the degree of cell wall impregnation. This effect is attributed to increased diffusion into the cell walls due to AzA melting. Because impregnation can be enhanced by heating alone, this approach is considered highly relevant for practical applications. One of the authors investigated the increased bulking of AzA and reported that the dimensional stability strongly depends on the heating temperature (Otsuka *et al.* 2022). They also suggested that esterification occurs when wood is heated at 140 °C (Otsuka *et al.* 2022). AzA has attracted considerable attention as a bio-based material for biodegradable polymers (Todea *et al.* 2021). Recently, esterification of wood has been explored for its potential as a thermoplastic material (Sejati *et al.* 2023, 2024; Zuo *et al.* 2026). However, these studies primarily addressed dimensional stabilization and did not provide detailed insights into the microstructural changes or the behavior of AzA during heating. The authors propose that a clearer understanding of the properties of AzA-esterified wood will enable applications, such as three-dimensional plastic flow molding (Yamashita *et al.* 2009; Miki *et al.* 2017; Abe *et al.* 2020; Seki *et al.* 2022), and bring this technology closer to practical implementation. One of the authors has previously reported that esterification improves the plastic flowability of wood (Abe *et al.* 2020). However, the process requires the use of strong alkali, raising concerns regarding safety. In contrast, AzA impregnation uses only ethanol as a solvent, and thus is considered to have very high biocompatibility and safety.

This study aimed to comprehensively elucidate the changes in physical properties and microstructure of azelaic acid-impregnated wood during thermal treatment and to propose an eco-friendly esterified impregnated wood material.

EXPERIMENTAL

Materials

Wood specimens were cut from the sapwood of a Japanese cedar (sugi, *Cryptomeria japonica*).

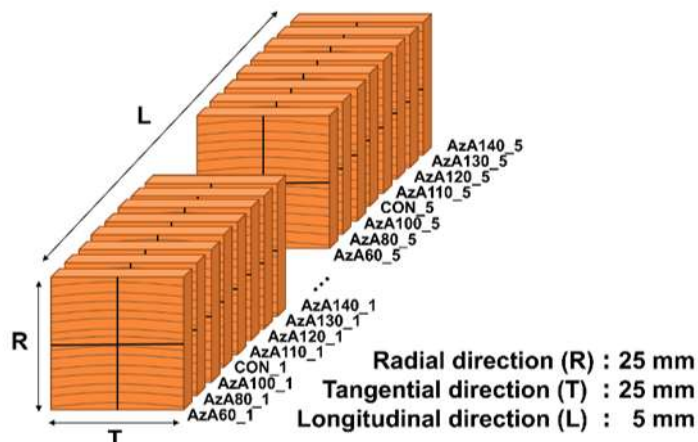


Fig. 1. A schematic diagram of sample preparation

All wood specimens were used without removing the native extractives. The specimens used for AzA impregnation were 5 mm (longitudinal, L) $\times$ 25 mm (radial, R) $\times$ 25 mm (tangential, T). A schematic of the sample preparation process is shown in Fig. 1. To maximize treatment efficacy and minimize specimen-to-specimen variation, AzA impregnation was performed using adjacent test specimens cut from the same piece of wood, as shown in Fig. 1. Measurement locations were adjusted to correspond to the same-growth ring regions during analysis.

Azelaic Acid Treatment

All reagents and solvents were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan) and used without further purification. The specimens were placed in a solution of 25 g of AzA dissolved in 75 g of ethanol, corresponding to a 25% w/w solution. The decompression was performed at a 100 hPa pressure for 30 min. After returning to atmospheric pressure, the wood was left in the solution for 24 h to complete impregnation. The specimens were then removed, excess solution was removed, and the wood was air-dried in a draft for at least 48 h. Subsequently, the wood was vacuum-dried at 35 °C for 48 h. Finally, the specimens were air-heated at predetermined temperatures (60, 80, 100, 110, 120, 130, and 140 °C) for 24 h to complete the impregnation process. These treated wood samples are hereinafter referred to as AzAx (where x represents the heating temperature), and the unheated wood is referred to as CON (control sample). The weight percent gain (WPG) and bulking were calculated using Eqs. 1 and 2,

$$\text{WPG (\%)} = (W_t - W_0) / W_0 \times 100 \quad (1)$$

$$\text{Swelling (\%)} = (T_t \text{ or } R_t - T_0 \text{ or } R_0) / T_0 \text{ or } R_0 \times 100 \quad (2)$$

where W_0 and W_t are the oven-dry weight (g) and the weight after azelaic acid treatment (g), respectively; and T_0 or R_0 and T_t or R_t are the oven-dry tangential or radial dimensions (mm) and the tangential or radial dimensions after AzA treatment (mm), respectively. The average of the five specimens was used in the results.

The ester content was calculated from the weight of the reactant grafted onto the specimens divided by the molecular mass of the hydroxyl substituted/OH ($W_{\text{OH}} = 17.0$ g/mol) as follows:

$$\text{WPG}_S = (W_{ts} - W_0) / W_0 \times 100 \quad (3)$$

$$\text{Ester content (mmol ester/g of dry wood)} = \text{WPG}_S / W_{\text{OH}} \times 1000 \quad (4)$$

where W_{ts} is the oven-dry weight (g) of the AzA-esterified wood after Soxhlet extraction with ethanol for 24 h.

Color Measurement

A spectrophotometer (CM-36dG, Konica Minolta, Inc., Japan) was used for color measurements. The measurements were conducted using a D65 illuminant and a 10° observer with a target mask (MAV: $\Phi 8$ mm). The measurement area was adjusted to include one annual ring using the supplied camera to account for the shading differences between earlywood and latewood. Color values were reported according to the CIELAB color system. L^* represents brightness on a scale of 0 to 100, whereas chromaticity is indicated by the a^* and b^* . The color difference (ΔE^*) in the CIELAB system was calculated as the Euclidean distance between points in the color space. Smaller ΔE^* values

indicate colors closer to the untreated sample, whereas larger ΔE^* values indicate greater color change. ΔE^* was determined using Eq. 5:

$$\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \quad (5)$$

The average of three measurements was used. Data extraction and analysis were performed using the accompanying software (SpectraMagic NX2 Version 1.30.006).

Compression Test

A small test piece (5 mm × 5 mm × 5 mm) cut from the wood specimens was subjected to a compression test (Autograph AG-X plus 20 kN; Shimadzu Corp., Kyoto, Japan; load cell SFL-20KNAG; Shimadzu Corp., Kyoto, Japan). It was set on a press surface that was heated to 170 °C and pressed in the R direction at a speed of 1 mm/min. The press was stopped when the force on the specimen reached 5 kN. The apparent compressive stress was calculated based on the initial surface area of the specimen. Measurements, including preliminary experiments, were repeated twice, and consistent results were obtained.

The appearance of the compressed sample from the LT planes was observed using an optical microscope (VHX-970F; Keyence Corp., Osaka, Japan). The deformed cross-sectional area of the LT planes before and after compression testing was calculated by binarizing the captured image, and the area magnification (AM_d) was calculated as follows,

$$AM_d = A_c / A_b \times 100 \quad (6)$$

where A_b and A_c are the areas of the deformed cross-sectional area of the dried sample before compression and the dried sample after compression, respectively.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed using a TMA7100 instrument (Hitachi High-Tech Co., Chiba, Japan). Measurements were conducted on small wood specimens (2.5 mm × 2.5 mm × 2.5 mm, L × R × T) prepared from AzA-impregnated wood. Each specimen was cut such that the latewood was sandwiched between earlywoods. During DMA, an oscillating compressive load of 200 ± 100 mN was applied in the radial (R) direction at 0.05 Hz, while the temperature was increased from 30 to 180 °C at a rate of 2 °C min^{-1} . The measurements were repeated twice, yielding consistent results. Data extraction and analysis were performed using accompanying software (TA7000 Standard Analysis).

Simultaneous Thermogravimetry/Differential Thermal Analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed using Seiko Instruments SII EXSTAR 6000 TG/DTA 6200 (Seiko Instruments, Chiba, Japan). Measurements were conducted on 1 to 5 mg samples placed in 5-mm aluminum pans under an air flow of 300 mL/min, with the temperature increased from 35 to 500 °C at a rate of 5 °C min^{-1} . Each specimen was cut such that the latewood was sandwiched between earlywood. All measurements were performed once. Data extraction and analysis were performed using accompanying software (TA7000 Standard Analysis).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a heat-flux differential scanning calorimeter (DSC Q200, TA Instruments). Measurements were

conducted on 1 to 5 mg samples placed in 4.5 mm aluminum pans under an N₂ flow of 300 mL/min, with the temperature increased from -10 °C to 200 °C at a rate of 5 °C min⁻¹. All measurements were performed once. Data extraction and analysis were performed using accompanying software (TA Instruments Universal Analysis 2000 for Windows 2000/XP/Vista Version 4.5A).

Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra were recorded using an FT/IR-4700 spectrometer (JASCO Co., Tokyo, Japan) at a resolution of 4 cm⁻¹ with 32 scans over the range of 500 to 4000 cm⁻¹. The attenuated total reflectance (ATR) data were collected using an ATR PRO ONE X instrument (JASCO Co., Tokyo, Japan) at ambient temperature. Attenuated total reflection infrared (ATR-IR) measurements were performed on the surface of the radial-tangential (RT) plane of the AzA-impregnated wood. Each measurement was repeated thrice, yielding consistent trends. Data extraction and analysis were performed using the accompanying software (Spectra Manager Version 2.15.2.1).

X-ray Diffraction (XRD)

An X-ray diffractometer (RIGAKU Series RINT-Ultima II, Tokyo, Japan) was used for all experiments. Measurements were conducted over a 2θ range of 5° to 40° at a scanning speed of 5° min⁻¹. Nickel-filtered CuK α radiation was employed, with the tube operated at 40 kV and a filament current of 40 mA. The specimens were positioned such that the X-rays were incident perpendicularly to the wood fibers (L-direction). Each measurement was repeated thrice, yielding consistent trends. Data extraction and analysis were performed using the accompanying software (PDXL 2, version 2.9.1.0).

RESULTS AND DISCUSSION

Structural Changes in Azelaic-acid-impregnated Wood

Figure 2a shows the swelling (bulking) of the AzA-impregnated wood after heating. AzA is a dibasic acid with a melting point of approximately 102 °C and exhibits temperature-dependent impregnation behavior (Otsuka *et al.* 2022).

Immediately after impregnation, all samples showed a WPG of approximately 65%. Heating below the melting point had little effect, whereas heating above the melting point reduced the WPG due to AzA leaching or evaporation. Swelling increased at higher temperatures, and AzA140 exhibited greater lateral swelling than the water-swollen control (6.6%). These results support previous findings that molten AzA leaches and redistributes into the cell walls (Itoh 1983; Otsuka *et al.* 2022), suggesting the presence of two forms of AzA in wood: one diffused into the cell walls and the other eluted outside the cells. Figure 2b shows the ester content of AzA-impregnated wood after heating. For AzA60 and AzA80 specimens, the ester content remained nearly zero, indicating that esterification did not occur under these conditions. In contrast, the samples heated above the melting point exhibited a progressive increase in ester content with increasing temperature. These results demonstrate that impregnation of wood with AzA using ethanol as a solvent alone was insufficient to induce detectable esterification between AzA and wood constituents (such as cellulose, which contains abundant hydroxyl groups), whereas heat treatment promoted ester formation. However, the values obtained in this study were considerably lower than the ester contents of fatty acids reported by Sejati *et al.* (2023, 2024).

Figure 2c and 2d shows the ATR-IR spectra of AzA-impregnated wood. AzA60 and AzA80 displayed typical AzA spectral features (Nattkemper *et al.* 2003), indicating surface coverage. All samples exhibited C=O stretching peaks at 1720 to 1700 cm^{-1} , with AzA140 also showing a peak near 1730 cm^{-1} . Because esterification shifts C=O stretching to higher wavenumbers (Smith 2018), these results indicate that esterification progressed with increasing temperature.

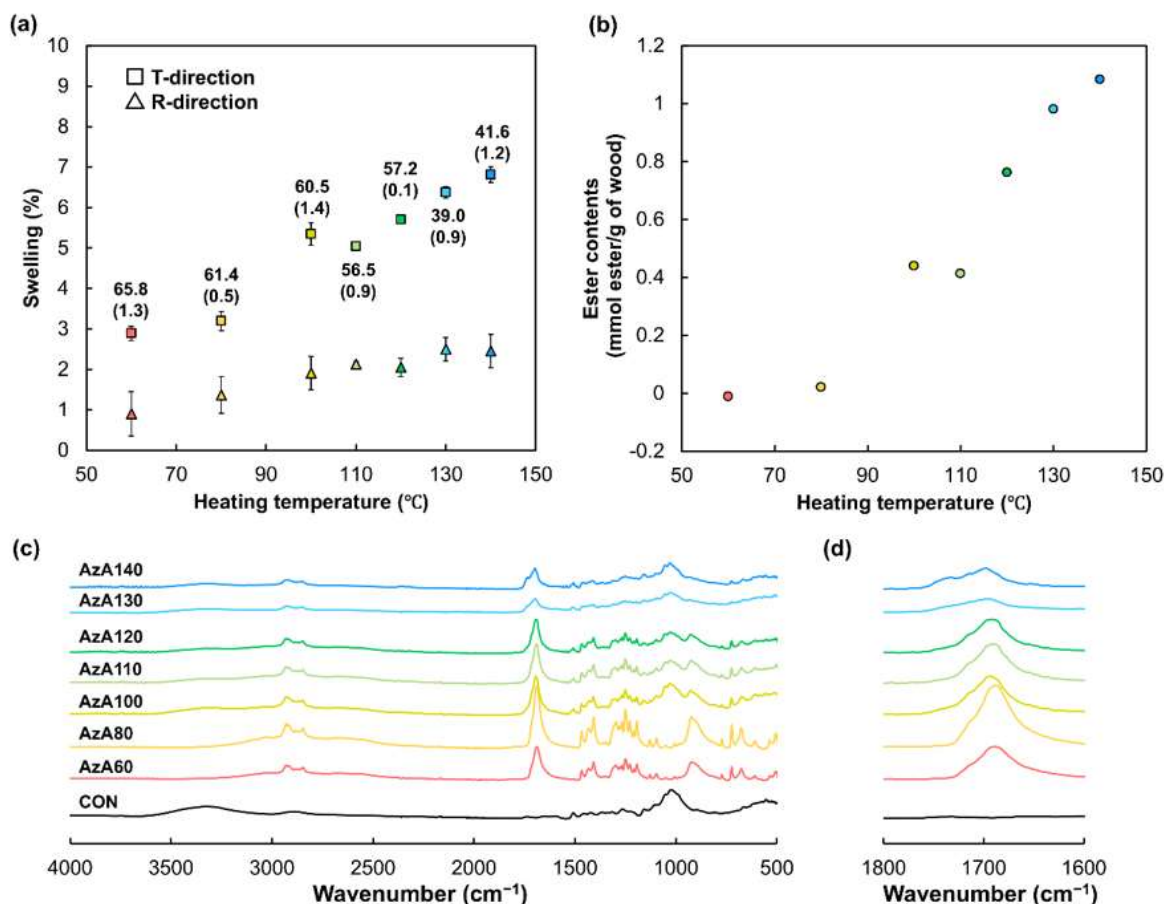


Fig. 2. Effect of heating temperature on swelling (a) and ester contents (b) of AzA impregnated wood; The numbers in the figure indicate the average WPG, while the numbers in parentheses indicate the standard deviation; ATR-IR spectra of AzA impregnated wood: (c) full range and (d) in the range from 1800 to 1600 cm^{-1}

Plastic Flow Properties of Azelaic-acid-esterified Wood

Figure 3 shows (a) photographs of AzA impregnated wood before and after compression, (b) the color difference (ΔE^*) induced by the impregnation treatment, and (c) the compression stress-strain curves. Below the melting point, surface AzA caused whitening and an increase in ΔE . Near the melting point, the AzA surface melted, restoring the natural wood color. Above its melting point, the wood darkened significantly and approached a brown hue. Figure S1 shows the color changes of AzA-impregnated wood upon heating. Figure 3c shows the relationship between the nominal compressive stress (σ) and the compression ratio (C) during compression testing for each specimen. For all samples, σ increased only slightly until C reached approximately 60%, during which the cell lumens gradually closed due to buckling of the cell walls. As C further increased, σ rose sharply, followed by the appearance of an inflection point where the rate of increase

in σ decreased (indicated by the black arrows in Fig. 3c). Before this inflection point, the cell lumens were completely closed and the samples became densified, resulting in a rapid increase in σ . After the inflection point, the rate of increase in σ decreased because the wood samples plastically deformed in the unconstrained direction (L or T). These compressive behaviors were similar to those reported in a previous study (Miki *et al.* 2017). It is worth mentioning that an inflection point was observed at approximately 10 MPa in the AzA140 sample (blue arrow). Although previous studies have reported that, in the case of propionylated wood, a region with a reduced slope in the σ - C curve appears at pressures of 30 to 50 MPa, the present results indicate that AzA esterified wood can undergo plastic deformation under substantially lower loads compared with conventional esterified wood (Abe *et al.* 2020). The area magnification (AM_d) also increased with increasing heating temperature, and the plastic flow in the T-direction was particularly pronounced. AzA bleeding was observed in specimens heated below the melting point, whereas no bleeding was observed in those heated above the melting point.

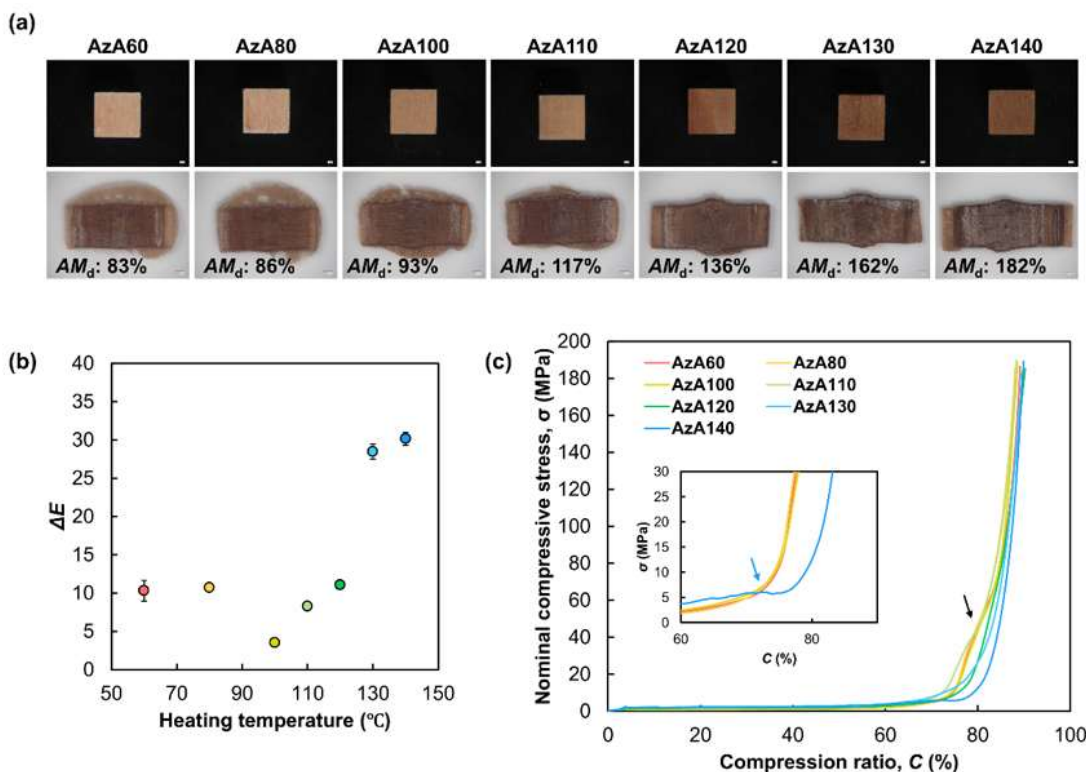


Fig. 3. (a) Photographs of AzA-impregnated wood before and after compression, (b) the ΔE induced by the impregnation treatment, and (c) the compression stress–strain curves

Thermal Softening Behavior of Azelaic-acid-esterified Wood

The temperature dependence of E'/E'_{50} and dL in the radial direction of AzA-impregnated wood at 0.05 Hz is shown in Figs. 4a and 4b. E' represents the storage modulus, and E'_{50} refer to the storage modulus measured at 50 °C. The quantity dL indicates the displacement of the specimen during the DMA measurement. Wood heated below or near the melting point of AzA exhibited two drops in E'/E'_{50} around 80 and 130 °C. In contrast, wood heated above the melting point showed only a slight decrease near 80 °C. The pronounced drop near 130 °C is attributed to esterification (Nakano 1994; Abe *et al.* 2020). All AzA-impregnated samples showed an increase in dL starting around 80 °C, with the

rate of increase greater at lower heating temperatures. This suggests AzA melted and redistributed into the cell wall during measurement (Fig. 2). The decrease in E'/E'_{50} near 80 °C is likely resulting from AzA transitioning to a liquid state and increased swelling due to impregnation, which is supported by the higher E'/E'_{50} values around 50 °C compared to the control (CON) (Fig. S2).

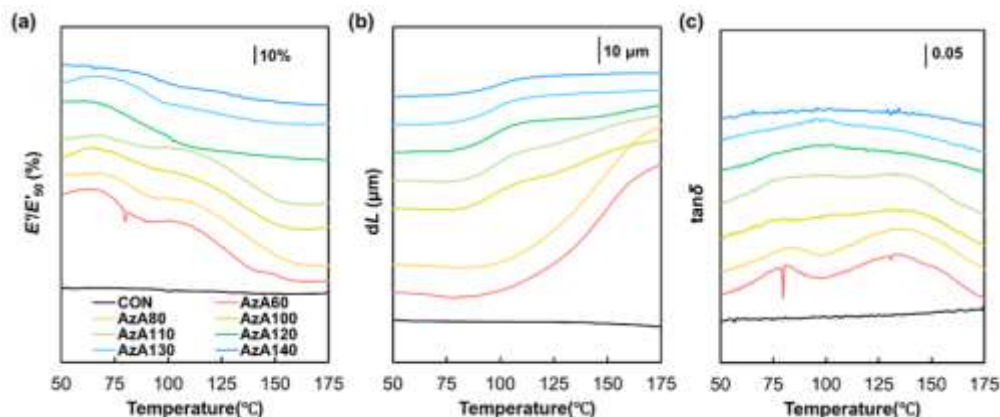


Fig. 4. Temperature dependence of E'/E'_{50} (a), dL (b), and $\tan\delta$ (c) in the radial direction of AzA impregnated wood at 0.05 Hz, where E'_{50} are E' at 50 °C

Figure 4(c) shows the temperature dependence of $\tan\delta$ in the radial direction of AzA-impregnated wood at 0.05 Hz. Samples heated below the melting point of AzA exhibited distinct peaks around 80 and 130 °C. In contrast, the samples heated near or above the melting point displayed broader merged peaks, with AzA140 showing no clear peaks. A similar behavior was reported for melamine-formaldehyde resin-impregnated wood (Seki *et al.* 2024).

Thermal Stability of Azelaic-acid-impregnated Wood

Figure 5 shows the TG curves of the AzA-impregnated wood.

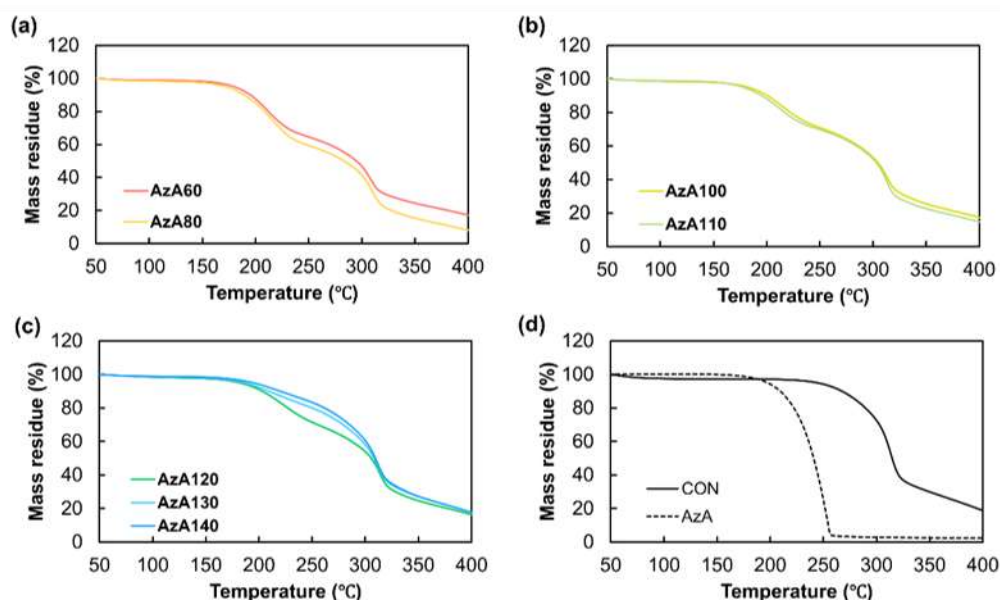


Fig. 5. The TG curves of the AzA impregnated wood

All samples exhibited less than 2% mass loss between 50 and 150 °C, followed by two major losses between 150 and 250 °C and 250 to 400 °C. The first loss was attributed to AzA decomposition and the second to the degradation of wood components. Notably, AzA130 and AzA140 showed minimal initial mass loss, possibly because of the lower AzA content or enhanced thermal stability resulting from reactions with wood.

Figure 6 shows the DTA curves and melting peak areas of AzA. All samples exhibited an endothermic peak near 100 °C, which decreased with increasing heating temperature. Although AzA130 and AzA140 showed approximately 40% weight gain (Fig. 1), their reduced melting peaks suggested that most of the AzA was in a non-melting state, which was likely due to esterification with wood components. Figure S3 shows the thermograms recorded by DSC together with the melting peak areas. All samples exhibited an endothermic peak near 100 °C, and the peak decreased with increasing heating temperature. For the CON sample, no thermal events were observed other than the endothermic signal associated with water evaporation in the range from minus 10 to 200 °C. Reduced melting peaks of AzA130 and AzA140 were also observed in the DSC measurements, suggesting that most of the AzA was in a non-melting state, likely due to esterification with the wood components.

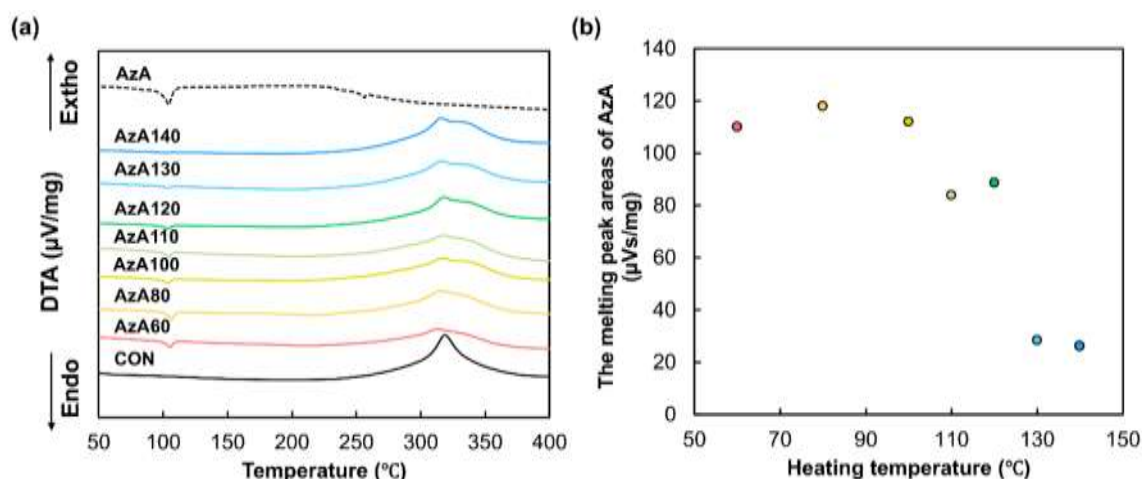


Fig. 6. The DTA curves (a) and the melting peak areas of AzA (b) in the AzA impregnated wood

Crystalline Structure of Azelaic-acid-impregnated Wood

Figure 7a shows the full-range XRD patterns of the AzA-impregnated wood. As reported previously (Su *et al.* 2020), AzA crystallized in ethanol exhibited α -type peaks at $2\theta = 9.7^{\circ}$ and 22.7° , and β -type peaks at $2\theta = 8.6^{\circ}$, 21.8° , and 23.3° . Both forms were observed in this study, but their intensities decreased with increasing heating temperature, and the β -form peak disappeared in AzA140. The β -form is considered more stable due to lower intermolecular interactions and conformational energy (Thalladi *et al.* 2000; Su *et al.* 2020) and has a more elongated lattice structure. Although this study did not confirm whether the β -form is more easily impregnated into wood, the observation is noteworthy. Figure 7b shows the peak position and full width at half maximum of the cellulose (200) lattice plane fitted with a Gaussian function (an example is shown in Fig. 7c). These parameters were similar to those of CON, indicating that the crystalline structure of the cellulose remained largely unchanged.

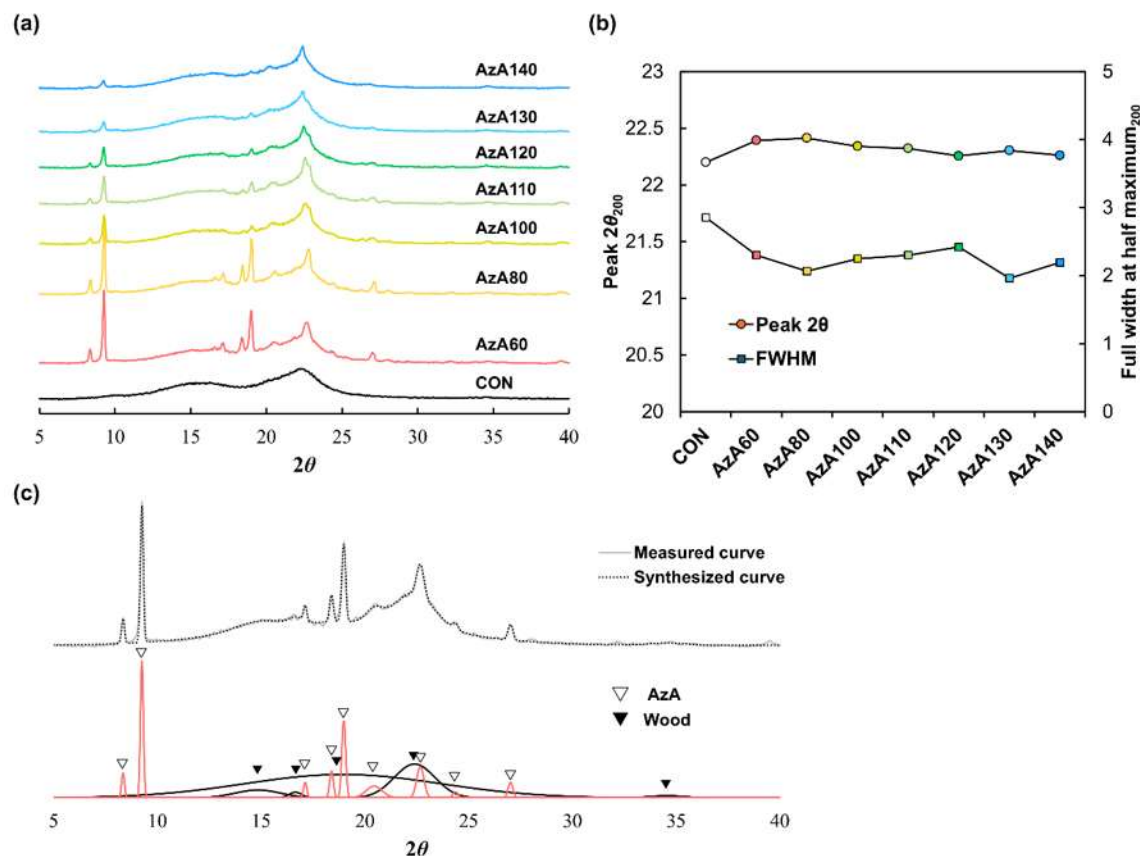


Fig. 7. XRD patterns of AzA impregnated wood: a: full range; b: Peak $2\theta_{200}$ and $FWHM_{200}$; c: An example of XRD pattern and Gaussian fitting of AzA-impregnated wood (AzA60)

General Discussion

Figure 2a shows that AzA-impregnated wood using ethanol as a solvent initially exhibited lower swelling, but the material swelled upon heating, which is consistent with previous studies (Itoh 1983; Otsuka *et al.* 2022). Figures 3b and 7a indicate that, at low temperatures, a substantial amount of unreacted AzA remained in the lumen or on the surface. Figure 2c, 2d shows that AzA esterified with wood components upon heating. However, as shown in Fig. 6b, some unreacted AzA persisted and did not contribute to the reaction. These findings were consistent with the ester content results shown in Fig. 2b. Although the reaction ratios for each wood component remain unclear, reports by Nakano (1994) and Sejati *et al.* (2024) suggest that most wood esterification occurs *via* reactions with cellulose. In the present study, while considering the possible reactions with lignin and hemicellulose, the authors focused discussion on their reactivity toward cellulose. It is worth mentioning that Fig. 7 reveals different crystalline polymorphs of AzA in wood, with the β -form preferentially disappearing upon heating. Because the AzA crystalline polymorphism depends on the solvent (Su *et al.* 2020), further investigation is needed to clarify its relationship with the impregnation behavior.

As shown in Fig. 4, two distinct peaks were observed in the $\tan\delta$ of AzA-impregnated wood. Nakano observed that in caprylated wood, dispersions at 130 °C (α), 60 °C (β), -20 °C (γ), and -70 °C (δ) become less distinct with increasing ester content, eventually leaving only β and δ (Nakano 1994). However, Sejati *et al.* (2023) reported that the longer the fatty-acid chain length, the lower the temperature at which the initial

deformation occurs, reflecting the melting point of the corresponding fatty acid. As shown in Fig. 2b, almost no esterification occurred for AzA60 and AzA80. Therefore, the softening behavior observed around 80 °C can reasonably be attributed to the melting of AzA. Similarly, long-chain fatty acids exhibit thermal softening around 150 °C, and because this temperature range does not overlap with the thermal-decomposition region of wood, the softening is considered to result from the modified wood matrix (Sejati *et al.* 2023). Accordingly, the peak observed near 130 °C in AzA-impregnated wood may be attributed to esterification of the wood constituents. For AzA60 and AzA80, *dL* increased markedly during the measurement, as shown in Fig. 4b. This suggested that esterification progressed during the measurement, resulting in the appearance of a peak. According to Sejati *et al.* (2023), the second thermal softening occurs predominantly in esterified cellulose and hemicellulose and is not observed in lignin. Figure 5 shows that AzA130 and AzA140 decomposed differently from the CON and AzA between 250 and 300 °C, reflected in the two-step exothermic behavior in Fig. 6a. The 320 °C peak in the CON is primarily due to cellulose pyrolysis (Zhou *et al.* 2015), while esterified cellulose and hemicellulose are known to exhibit enhanced thermal stability (Sejati *et al.* 2024). Unlike previous studies that used swelling solvents, no decrease in cellulose crystallinity was observed in this study, likely because of the limited swelling effect of ethanol (Sejati *et al.* 2023). Further clarification requires isothermal and low-temperature viscoelasticity measurements.

The most important finding of this study is that although no distinct $\tan\delta$ peak was observed for AzA140, this sample exhibited excellent flow properties. In other words, AzA140 can be regarded as a state in which thermal softening is suppressed, yet plastic flow occurs readily. The disappearance of the $\tan\delta$ peak around 80 °C can be explained by the reduction of unreacted AzA within the AzA-impregnated wood, as shown in Fig. 6b. As shown in Fig. 6, heating above 120 °C enhanced thermal stability, suggesting esterification of cellulose and hemicellulose; thus, the disappearance of the peak around 130 °C is likely attributable to cross-linking. Similar dual cross-linking behavior has been reported for tetracarboxylic acids (Zuo *et al.* 2026).

Meanwhile, flow phenomena have been attributed to selective softening of the intercellular layer, which induces slippage, as previously reported (Miki *et al.* 2017). It is well known that the intercellular layer contains a high concentration of lignin. Therefore, the enhanced flow behavior observed in this study may be associated with esterification of lignin within the intercellular layer, although direct evidence was not obtained in this study. A 2D-NMR study has demonstrated that glutaric acid, a dicarboxylic acid, can react with lignin in wood (Ando *et al.* 2025).

Overall, the DMA measurements clarified the temperature-dependent viscoelastic changes in AzA-impregnated wood and indicated the possibility of esterification and cross-linking reactions involving cellulose, although these mechanisms were not directly verified in the present study. While the dimensional stability of AzA-impregnated wood has previously been attributed to bulking and hydrophobicity resulting from esterification, the present findings suggest that cross-linking also contributes to its high dimensional stability (Itoh 1983; Otsuka *et al.* 2022). In contrast, based on the results of the compression tests, esterification of lignin may also play a non-negligible role. A limitation of this study is that it remains unclear at present whether AzA is uniformly distributed within the wood cell walls and the intercellular layer. One hypothesis is that esterification increases the hydrophobicity of the cell wall, thereby promoting the diffusion of AzA. Verification of

this hypothesis will require visualization of the AzA distribution within the cell wall using techniques such as Raman imaging analysis.

A key outcome of this study is that, unlike conventional esterified wood, AzA-impregnated wood can exhibit both thermoplastic and thermosetting behaviors depending on the heating temperature. This dual behavior is expected to improve formability through thermoplastic flow while enabling shape fixation through thermosetting, making it advantageous for applications such as three-dimensional plastic flow molding (Yamashita *et al.* 2009; Miki *et al.* 2017).

CONCLUSIONS

1. Azelaic acid (AzA)-impregnated wood heated below the melting point of AzA revealed that unreacted AzA was present on the bulk surface and in the lumen, and heating above the melting point resulted in diffusion into the cell wall and esterification.
2. Heating at 120 °C or higher may promote the formation of cross-links between molecular chains in the AzA-impregnated wood by thermal and viscoelastic behavior.
3. The nominal compressive stress (σ)–compression ratio (C) curve exhibited an inflection point at approximately 10 MPa, suggest sliding behavior in the intercellular layer under low compressive loads.
4. Unreacted AzA was present in all the samples, and different crystalline polymorphs of AzA were observed.

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Conflict of Interest

The authors declare that they have no competing interests.

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APPENDIX

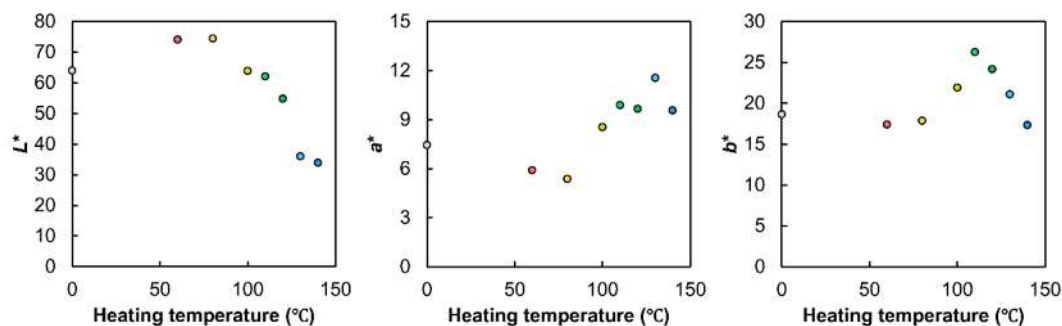


Fig. S1. Effect of heating temperature on color change (L^* , a^* , b^*) in the AzA impregnated wood; Untreated wood (CON) was plotted as a heating temperature of 0 °C

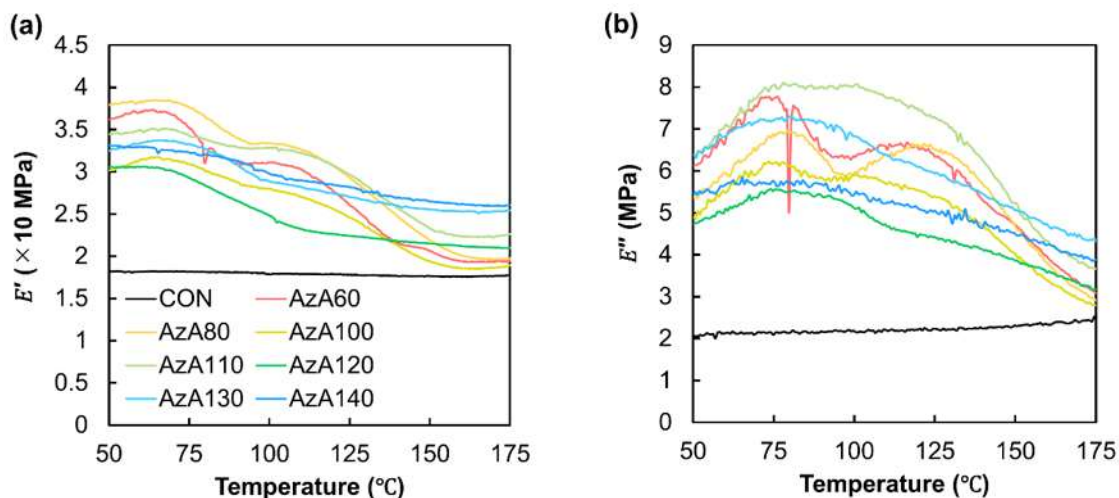


Fig. S2. Temperature dependence of E' and E'' in radial direction of AzA impregnated wood at 0.05 Hz

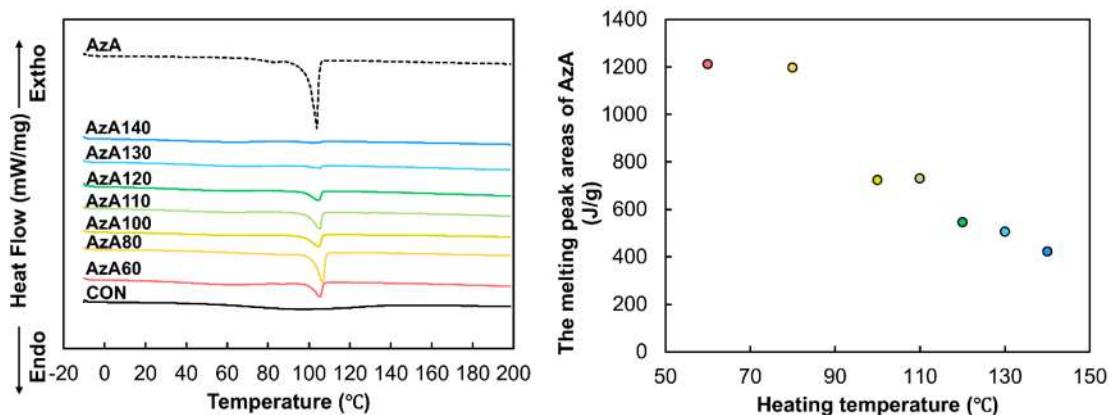


Fig. S3. Thermogram recorded by DSC of AzA impregnated wood (a) and the melting peak areas of AzA (b) in the AzA impregnated wood