Polymer Testing 154 (2026) 109061

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytest

Characterization of delignified woods modified with ε -caprolactone

Şeyma Özlüsoylu [a], Ahmet Can [b,c], Sauradipta Ganguly [d,*]

[a] Institute of Graduate Education, Bartin University, 74100, Bartin, Türkiye
[b] Bartin University, Forest Products Application and Research Center, 74100, Bartin, Türkiye
[c] Department of Forest Industrial Engineering, Bartin University, 74100, Bartin, Türkiye
[d] Natural Resources Institute Finland (LUKE), Production Systems, Joensuu, 80100, Finland

ARTICLE INFO

Keywords:
Deep eutectic solvent
Delignification
ε-caprolactone (ε-CL)
Wood modification

ABSTRACT

This study explores the use of deep eutectic solvents (DES) for selective lignin removal from wood, followed by in situ polymerization of ε-caprolactone (ε-CL) to enhance structural and functional properties of wood. Scots pine (*Pinus sylvestris L.*) and beech (*Fagus orientalis*) were treated with DES formulations based on choline chloride (ChCl) combined with oxalic acid (OA) or glycerol (GL) at molar ratios of 1.5:1 or 1:1, respectively. Post-treatment, ε-CL was grafted onto the delignified wood via ring-opening polymerization. Beech specimens treated with OA-based DES exhibited high mass loss and low weight percent gain (WPG: 60 %) which was different for Scots pine where lower mass loss and higher WPG (143.45 %) was observed, possibly indicating a more efficient CL grafting. The modified wood of both the species, exhibited improved water resistance and dimensional stability, with swelling values below 10 % and remarkably reduced water uptake rates. Anti-swelling efficiency exceeded 54 % in beech and 35 % in pine. FTIR confirmed successful CL grafting through ester carbonyl bands, while XRD indicated reduced crystallinity, suggesting increased amorphous character; potentially justifying the use of DES-assisted delignification and CL polymerization for functional wood modification.

1. Introduction

Wood is widely recognized as a sustainable, bio-based construction material due to its excellent mechanical properties, ease of processing, and natural aesthetic appeal. However, its cellular structure is composed primarily of three biopolymers; cellulose, hemicellulose, and lignin, which contain a high density of accessible hydroxyl (-OH) groups. These polar functional groups readily form hydrogen bonds with water molecules, rendering wood inherently hygroscopic [1]. As a result, wood absorbs and desorbs moisture in response to changes in ambient humidity, leading to dimensional instability known as swelling and shrinkage in use. This moisture-driven behavior can further contribute to crack formation and propagation, moisture induced degradation, and increased susceptibility to microbial attack, thereby limiting wood's long-term durability in service environments [2]; [3–5]. To overcome these limitations associated with the use of wood in service, several wood modification techniques have been developed and adopted over the years. Chemical wood modification practices primarily aim to reduce the hygroscopicity and enhance the durability of woody biomass by altering its chemical structure [6]. These processes typically involve the substitution, blocking or masking of accessible hydroxyl (-OH) groups; primarily found in cellulose and hemicellulose, with hydrophobic functional groups [7]. By reducing the number of sites available for hydrogen bonding with water molecules, such modifications significantly increase water repellency, improve dimensional stability, and enhance resistance to biological degradation, including fungal and microbial attack. This approach is fundamental to extending the service life of wood in moisture-prone environments [2]; [1]. In recent years, within the framework of environmentally friendly approaches, modifications using biodegradable polymers, particularly polycaprolactone (PCL), have attracted attention. The in-situ binding of PCL to wood cell walls via ring-opening polymerization significantly reduces water uptake and dimensional changes, while also increasing resistance to decay and environmental stressors that escalate it [4,8].

Recent studies have already demonstrated the high efficiency of deep eutectic solutions (DES) in the structural conversion of lignocellulosic biomass. Morán-Aguilar et al. [9] reported that pretreatment of sugarcane and beer bagasse with choline chloride/glycerol-based DES resulted in the removal of 80 % of acid soluble lignin and 15 % of Klason lignin, thus significantly increasing saccharification efficiency. Zhou

---

* Corresponding author.
E-mail address: sauradipta.ganguly@luke.fi (S. Ganguly).

https://doi.org/10.1016/j.polymertesting.2025.109061
Received 13 October 2025; Received in revised form 20 November 2025; Accepted 27 November 2025
Available online 27 November 2025

et al. [10] achieved almost complete cellulose conversion with over 90 % delignification and xylose removal in a short time with the p-toluene sulfonic acid/choline chloride system. Li et al. (2022) emphasized that neutral DES systems (e.g., choline chloride/glycerol) only altered the lignin structure to a limited extent, whereas urea-based DESs initiated partial depolymerization–repolymerization processes by breaking β–O–4′ bonds. In addition, Shen et al. [11] reported that bamboo treated with DES formed closed-pore hard carbon anodes after carbonization and exhibited high electrochemical performance, showing that DES also has potential in energy storage materials. On the other hand, several studies such as Huang et al. [12] and Liu et al. [13], also focused on the reuse potential of DES systems; Huang et al. [12] reported that the lignin removal rate decreased from 79.08 % to 30.30 % after three cycles, while Yao et al. [14] reported decrease from 80 % to 60 % in the third cycle. In the ultrafiltration method widely used in DES recovery, Ippolitov et al. [15] purified the choline chloride/lactic acid system through cellulose membranes and removed 95 % of lignin and hemicellulose after two-stage filtration. Recently, Ma et al. [16] achieved high bonding rates and improved mechanical strength by nanofibrillating wood components using a DES system containing LA/ChCl/ε-caprolactone and polymerizing ε-CL in the same environment in a single step. Similarly, Huang et al. [17] developed super-hard wood composites inspired by natural lignification. All these studies demonstrate that DES-based delignification not only facilitates lignin removal but also facilitates the diffusion and covalent bonding of polymer systems such as ε-caprolactone into the wood matrix. In this context, the primary purpose of delignification in our current study was not to directly impart hydrophobicity but to facilitate chemical modification with ε-CL by increasing the reactivity of hydroxyl groups present in wood.

ε-caprolactone (ε-CL), an aliphatic, biodegradable polyester monomer with suppressed hydrophilicity, is gaining increasing attention in wood modification in recent years. ε-CL undergoes ring-opening polymerization with the hydroxyl groups in the wood cell wall, forming poly (ε-caprolactone) (PCL) chains. These chains are covalently bonded to the wood polymers, significantly reducing the surface's polarity and imparting water-repellent properties. Consequently, the temporarily increased hydrophilicity after delignification is offset by the chemical hydrophobization process that occurs during PCL modification. This reaction is typically carried out in the presence of a Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) catalyst that provides high-yield polymerization at lower temperatures, allowing the modification to occur without damaging the wood structure. As a result of this modification, significant improvements are observed, particularly in the water repellency and dimensional stability of wood [2], [18,19]. Ring-opening polymerization of ε-CL is generally carried out using metal-based catalysts [20]. However, enzymatic and organic catalytic systems can also be used for this purpose [21]. The -OH groups of carbohydrates such as cellulose; serve as components that initiate the polymerization of ε-caprolactone by opening the ring structure, and thus cellulose grafted with PCL is obtained [22,23]. In situ polymerization of wood with ε -caprolactone has been studied since 2014 and quite successful results have been obtained [2]; [18,19]. In this process, the penetration of ε -caprolactone into the wood cell wall is a critical step for the effectiveness of the modification and therefore, solvents such as dimethylformamide are used as swelling agents to ensure the swelling of the wood structure [2]; [4]. Hydrophobic PCL chains infiltrate the wood's porous structure, impeding water diffusion and thereby reducing moisture-induced swelling and shrinkage. Additionally, PCL's strong interfacial compatibility with wood preserves the composite's mechanical integrity, enhancing its resistance to outdoor weathering. Therefore, modifying wood with PCL represents a sustainable and efficient strategy to counteract its inherent hygroscopicity [24–26], with exiting literature already reporting that grafting PCL onto wood cell walls significantly enhancing both water resistance and dimensional stability [2].

Although many studies have separately addressed the use of DES or ε-CL in wood modification, no research till date has evaluated the combined use of DES-assisted delignification followed by CL modification and their synergistic impact. Most of the existing studies in literature have focused either solely on the removal of lignin with environmentally friendly solvents or on the polymerization of CL within the wood matrix; however, the synergistic effects that could arise from the sequential application of these two processes have not been sufficiently investigated. DES-induced delignification reduces the amount of lignin in the wood cell wall, increasing porosity and diffusion pathways [27], thus possibly enabling deeper penetration of the CL monomer into the wood matrix; ensuring more efficient polymerization. This potential synergy, therefore, is expected to not only increase modification efficiency but also improve performance parameters such as dimensional stability, water repellency, and biological durability. Previous studies have reportedly used toxic and environmentally undesirable solvents (e. g., N,N-dimethylformamide, DMF) [4], limiting the sustainability and applicability of the process. Therefore, controlled CL modification following effective lignin removal with DES is considered to have the potential to fill a large gap in the literature and establish it as a more environmentally friendly and effective wood processing method.

The main objective of this study was to investigate the effects of ε-caprolactone (CL) grafting on the structural and thermal properties of DES-pretreated wood specimens (DW-OA and DW-GL). In this context, wood specimens with reduced lignin content and increased porosity were modified by polymerizing with CL, and the performance of the resulting composites were evaluated using advanced characterization techniques such as thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). Furthermore, it was hypothesized that the modification process would contribute to amelioration of fundamental engineering properties like dimensional stability, enabling the development of environmentally friendly, high-performance wood-based materials.

2. Materials and methods

2.1. Materials

For dimensional stability tests, boards of Scots Pine (*Pinus sylvestris* L.) and Beech (*Fagus orientalis*) were converted into specimens of dimension 20 mm (Radial) x 20 mm (Tangential) x 10 mm (longitudinal). FTIR, TGA, and XRD analyses were also performed on powdered samples obtained by grinding the specimens prepared at this size. Choline chloride (Ch, 139.62 g/mol, ACROS, 99 %), oxalic acid (OA, 126.07 g/mol, Merck), and glycerol (GL, 92.09 g/mol, Merck) were used in the delignification process. ε -caprolactone (CL, 114.14 g/mol, Merck, 99 %), tin (II) ethylhexonate used as catalyst and acetone (99 %) were purchased from Alfa-Aesar (Haverhill, Massachusetts, USA).

2.2. Delignification of wood

Deep eutectic solvents (DES) are chemical mixtures containing a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) in which two or more components are combined in solid or liquid form and interact via hydrogen bonding. Various DESs were prepared by combining OA and GL with ChCl. The mixing process was carried out according to the method specified in our previous study [28]. The mixtures prepared in a molar ratio of 1:1.5 for OA: ChCl [28] and 1:1 for GL: ChCl [29], were stirred with a magnetic stirrer in a water bath at 90 °C. The mixtures obtained were clear and homogeneous solutions, and no precipitate was formed after cooling to room temperature.

In our previous study [28], the process of applying DES prepared with OA and GL to wood specimens was detailed. Similarly, in this study, wood specimens, each with dimensions of 20 mm × 20 mm × 10 mm, were kept in separate beakers containing 50 g of DES at 90 °C for one month. Then, at the end of the pretreatment period, the specimens were washed 6 times with a mixture of ethanol/water (25 mL, 1:1 M ratio) by changing ethanol/water twice a day for 3 days in order to completely remove the remaining DES on them. The extended exposure time was selected because DES systems exhibit inherently slow diffusion kinetics and high viscosity, requiring prolonged treatment to achieve sufficient penetration and effective delignification throughout the entire specimen thickness. Therefore, shorter treatment durations were not considered in this study. At the end of the process, the specimens were dried under a vacuum. The specimens that underwent delignification with OA were named as DW (b,p)-OA, and the specimens that underwent delignification with GL were named as DW (b,p)-GL (see Fig. 1).

2.3. Polycaprolactone modification

In this study, control and delignified wood specimens were modified by making some changes to the method reported by Ermeydan et al. [2]. In the modification process, 3 % tin (II) 2-ethylhexanoate was added to ε-caprolactone as a catalyst. The resulting solution was homogenized with a magnetic stirrer at 200 rpm for 30 min. Then, the prepared solution was poured onto wood specimens with dimensions of 20 × 20 × 10 mm, and those were kept under a 650 mm Hg vacuum for 30 min, and then the impregnation process was carried out by waiting atmospheric pressure for 24 h. The ratio between ε-caprolactone and wood was approximately 5 mL of monomer per specimen (20 × 20 × 10 mm, about 2.5 g). The monomer was used in its pure form without any solvent addition. The impregnated specimens were wrapped with aluminum foil for polymerization (curing) and kept in the oven at 110 °C for 18 h (Fig. 1). After the curing process, the wood specimens were washed with acetone for 20 min and then with pure water for 20 min to remove monomer and catalyst residues remaining on the surface. The polymerization efficiency, expressed as the weight percent gain (WPG), was determined and discussed in the Results section to evaluate the amount of ε-caprolactone incorporated into the wood structure. Polycaprolactone modified specimen groups were defined and numbered in three different ways. Control specimens treated only with CL were named as beech or pine Control + CL. Specimens treated with oxalic acid based deep eutectic solution (DES), delignified and then modified with CL were named as DW (b,p)-OA + CL, and specimens treated with glycerol based DES, delignified and modified with CL were named as DW (b,p)-GL + CL. This definition was used in the comparative evaluation of specimen groups in all analyses. Pictorial representations of the prepared specimens are given in Fig. 2.

2.4. Mass loss (ML, %) and weight percentage gain (WPG, %)

In order to determine the changes in mass caused by the modification processes, the dry weights of the specimens were measured before and after each process. After the DES treatment, the mass loss values that occurred due to the removal of extractive and lignin-like components from the wood cell walls were calculated. After the polycaprolactone modification, Weight Percentage Gain (WPG) values were calculated to determine the amount of monomer taken into the specimens. These calculations were made to quantify the extent of modification on specimens subjected to individual treatments.

2.5. Anti-swelling efficiency (ASE, %), water uptake (WU, %), swelling (S, %), weight loss (%)

Initial dry weights and dimensions of all the specimens belonging to each treatment groups were recorded. Then, the specimens were submerged in pure water for 5 days. At the end of this period, weight and dimensions of the swollen specimens were recorded. Then, the specimens were acclimatized at room temperature for 24 h and dried in an oven at 103 ± 3 °C for 24 h and weight and dimensional measurements were taken again (first water immersion-drying cycle). This process was repeated for a total of three cycles; in each cycle, weight and dimensional measurements were made of both water-saturated and dried Specimens (8 steps in total). Using the obtained data, resistance to swelling (Anti-Swelling Efficiency, ASE, %), volumetric swelling coefficient (S, %), and weight loss (%) were calculated according to the

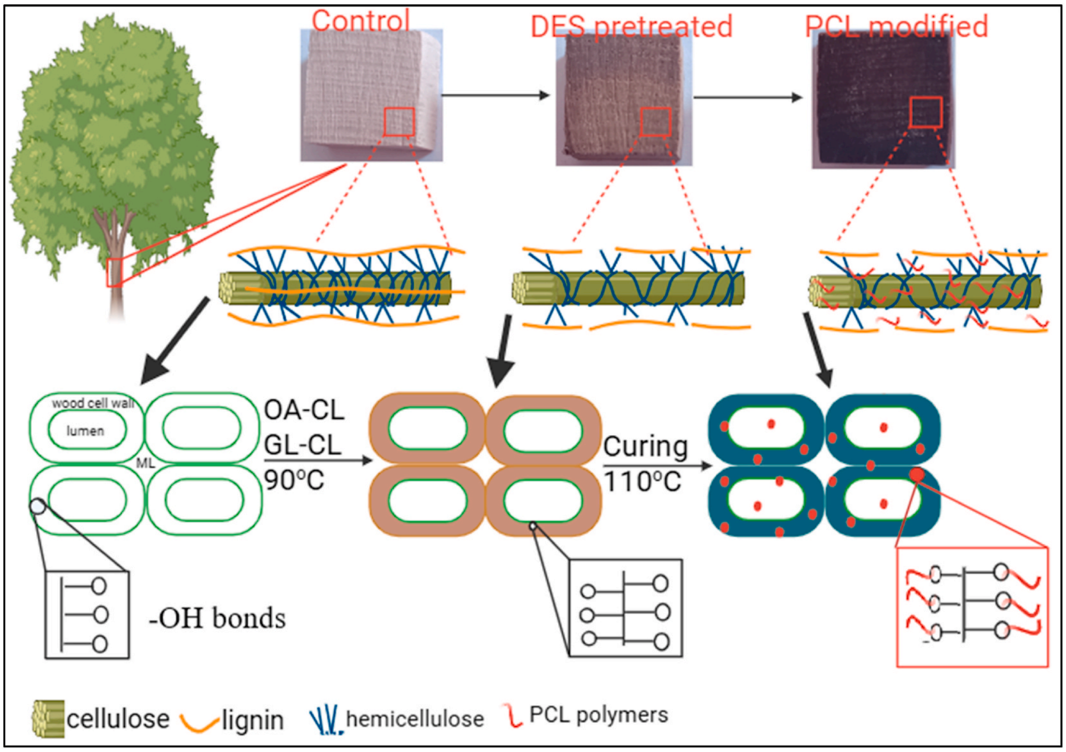

Fig. 1. Schematic illustration of the preparation process of PCL-modified wood pretreated with Deep Eutectic Solvent (DES). In the first step, wood specimens were impregnated with DES and kept in an oven at 90 °C for one month to promote lignin solubilization and partial depolymerization. After removing residual chemicals by gentle washing, the DES-treated specimens were subsequently modified with polycaprolactone via in-situ polymerization. "Image Created with BioRender.com".

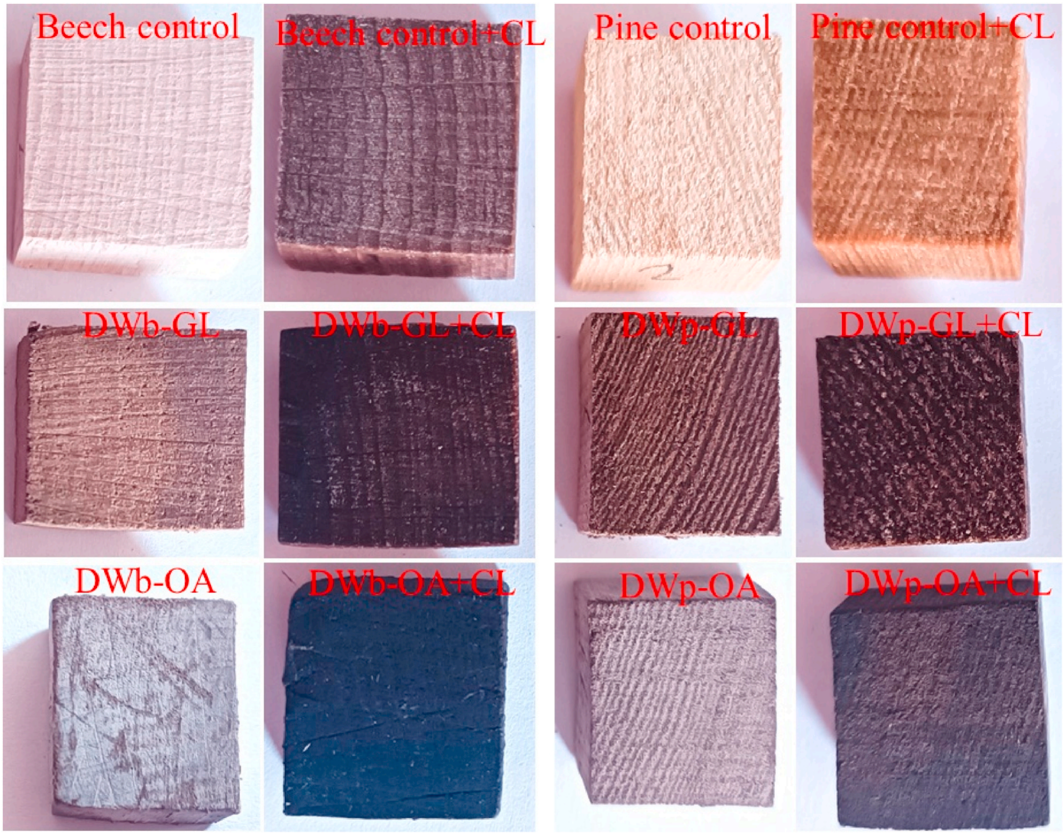

Fig. 2. Representation of beech and pine wood specimens before and after DES pretreatment and PCL modification.

method previously reported in the literature Ermeydan et al. [2]. Five replications for each treatment were used in the water uptake test and the mean values are reported.

2.6. Determination of chemical changes with FTIR spectra

The chemical structures of wood, and modified wood were analyzed using Fourier-transform IR analysis (Shimadzu IRAffinity-1, USA). Four accumulated spectra with a resolution of 4 cm^{-1} were obtained for wavenumbers ranging from 700 to 4000 cm^{-1} by performing 32 scans for each wood specimen.

2.7. Thermal stability analysis (TGA)

Thermal degradation behaviors of wood, and modified wood were examined using TGA device (P PerkinElmer TGA7; USA). An aluminum oxide crucible holding about 3 mg of powdered sample was subjected to heating and cooling from 24 °C to 800 °C at a rate of 10 °C per minute in argon atmosphere.

2.8. Crystalline structure analysis (XRD)

The crystal structure of the developed composites and their constituents were determined by an XRD device (PANalytical X'Pert^3 powder diffraction device, USA) operating under 40 mA and 45 kV conditions under Cu radiation source. Measurements were performed on powdered samples to ensure homogeneous diffraction and accurate crystallinity determination. The crystallinity index (% CrI) was calculated using the peak height method proposed by Segal et al. [30]. This calculation was performed by dividing the difference between the peak intensity ($I_{(200)}$) of the (200) plane of the crystal observed at the angle $2\theta = 22.7^\circ$ and the minimum intensity value (I_{am}) corresponding to the amorphous region at $2\theta = 18.6^\circ$ by the ratio of $I_{(200)}$ (Supplementary Information, Table S1). The percentage of crystallinity was expressed by the following equation (1):

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \, x \, 100 \tag{1}$$

2.9. Statistical analysis

The water uptake results were analyzed by the simple and multivariate analysis of variance (ANOVA) in IBM SPSS 16 statistical software, and test methods were classified by Duncan groups ($p < 0.05$). Step and cycle were not examined in themselves. Only variations were compared with each other according to the final situation.

3. Results and discussion

3.1. Mass loss (ML, %) and weight percentage gain (WPG, %)

In Fig. 3, the mass loss (%) obtained after DES process and the percentage weight gain (WPG%) after CL modification values are presented and analyzed. It can be seen that beech (*Fagus orientalis*) and Scots pine (*Pinus sylvestris*) specimens exhibit different behaviors. In Scots pine, the mass loss after DES process is lower (DWp-GL: 9.05 %, DWp-OA: 11.65 %), whereas the WPG values after CL modification are quite high (DWp-OA + CL: 143.45 %, DWp-GL + CL: 159.91 %). This shows that pine wood largely preserves its structural integrity during DES process, allowing CL agents to penetrate deeper and more efficiently. In particular, the low density, high porosity, and permeability of pine wood make it more suitable for this type of modification. In beech specimens, mass loss after DES process is higher (DWb-GL: 17.06 %, DWb-OA: 26.75 %), but WPG values are lower compared to Scots pine (DWb-OA + CL: 60.0 %, DWb-GL + CL: 70.55 %). This situation suggests that the denser and more closed structure of beech wood makes it difficult for chemical

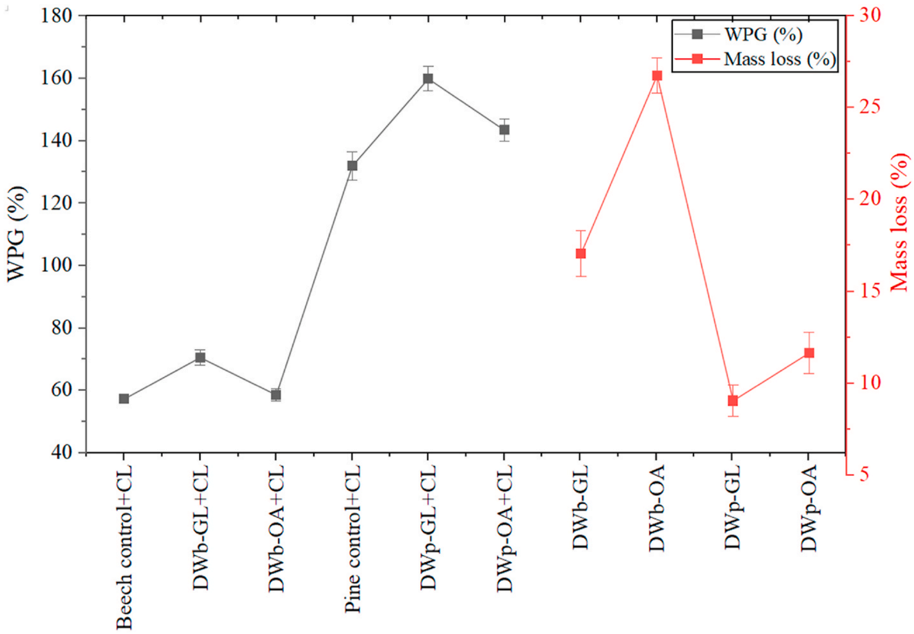

Fig. 3. Effect of different DES systems on Mass Loss (%) and WPG (%) after PCL modification in Beech and Scots Pine wood specimens.

substances to penetrate deeply into the cell wall. The higher dissolution of lignin and hemicellulose components during DES process increased mass loss in beech, but this structural disruption did not create sufficient binding points for CL molecules. Therefore, despite the high mass loss rate, WPG values remained low compared to pine. Also, delignification was observed to be more homogeneous in beech samples, whereas the process remained more superficial in Scots pine samples. This is particularly evident from the differences in mass loss data.

Data analysis in general revealed that the OA (oxalic acid) based DES system exhibited a more aggressive solvent behavior in both beech and pine woods. This system causes a more efficient dissolution of cell wall components (e.g. hemicellulose and lignin), leading to higher mass loss and lower binding sites in the wood tissue. These binding sites allow less reactive sites to be used during subsequent CL modification, resulting in lower WPG values. In both beech and Scots pine specimens subjected to DES treatment, WPG values obtained after CL modification were higher compared to control + CL samples. This situation shows that DES application partially opens or modifies the wood cell wall structure, creating more reactive sites where CL agents can bind. Especially, when treated with more aggressive DES systems such as OA, more dissolution occurs in cell wall components, which increases crosslinking capacity. As a result, DES pretreatment can be considered as a preliminary step to increase the effectiveness of CL grafting. This finding reveals that DES systems provide a functional surface and optimizes structure preparation in wood modification processes.

As reported by Li et al. [31], DES pretreatment partially solubilizes lignin and hemicellulose in the wood cell wall, disrupting lignin-carbohydrate complexes and making the cell wall more porous, permeable, and chemically reactive. As DES weakens ether bonds and loosens the lignin matrix, new hydroxyl groups are exposed on the cellulose and hemicellulose surfaces, creating active sites for subsequent chemical modifications. SEM images show that lumens widen and the middle lamella partially dissociate after DES treatment, creating an open microstructure that allows ε-caprolactone monomers to diffuse more easily into the cell wall. This structural transformation increases the efficiency of in situ polymerization and allows the free phenolic and aliphatic –OH groups; released during lignin removal, to interact with the ring-opening reactions of caprolactone to form covalent bonds through esterification. Furthermore, hydrogen bonds formed between the aromatic hydroxyl groups remaining in the lignin structure and the polymer chains enhance the dimensional stability and mechanical strength of the modified wood. Consequently, the lignin-removing effect of DES not only increases porosity but also creates a comprehensive chemical synergy, allowing the ε-CL chains to adhere more strongly to the wood matrix through both hydrogen bonding and covalent bonding [31,32].

3.2. Dimensional stability

The effect of polycaprolactone modification following different delignification pretreatments on the dimensional stability of beech wood was evaluated through ASE (Anti-Swelling Efficiency), water uptake (%) and swelling (%) and the values are presented in Fig. 4.

In the control group, in specimens modified only with CL, the ASE value decreased from 57.52 % in the first cycle to 44.70 % in the sixth cycle, indicating that CL partially binds to wood cell walls and provides water resistance, but this activity decreases marginally with cyclic aging. In DWb-GL specimens delignified with glycerol-based DES but not modified with CL, negative ASE values were observed in all cycles (e.g., Step 2: −44.16; Step 6: −39.14), indicating that lignin removal renders the structure more hydrophilic, reducing swelling resistance. In contrast, ASE values were positive in DWb-GL + CL specimens that underwent the same pretreatment and were subsequently modified with CL (Step 1: 57.70 %; Step 6: 42.74 %), demonstrating more effective binding of CL within the structure with reduced lignin content. The extremely negative ASE values (Step 1: −76.61 %; Step 6: −70.57 %) observed in DWb-OA specimens treated with oxalic acid-based DES indicate that stronger delignification significantly weakened the water resistance of the wood. However, in the DWb-OA + CL group, positive and stable ASE values (Step 1: 49.56 %; Step 6: 54.43 %) were obtained throughout all cycles after CL modification, indicating successful grafting of polycaprolactone onto the delignified wood cell walls, that significantly increased dimensional stability. These findings are consistent with similar studies in the literature and are similar to the ASE increases of up to 60 % in solvent-cured specimens reported by Ermeydan et al. [4]. The results of the present work therefore ascertain that polymeric integration of polycaprolactone into the wood structure is an effective method for increasing its water resistance.

In the beech control, high water uptake rates were observed throughout the three cycles (Cycle 1: 65.48 %; Cycle 2: 68.70 %; Cycle 3:

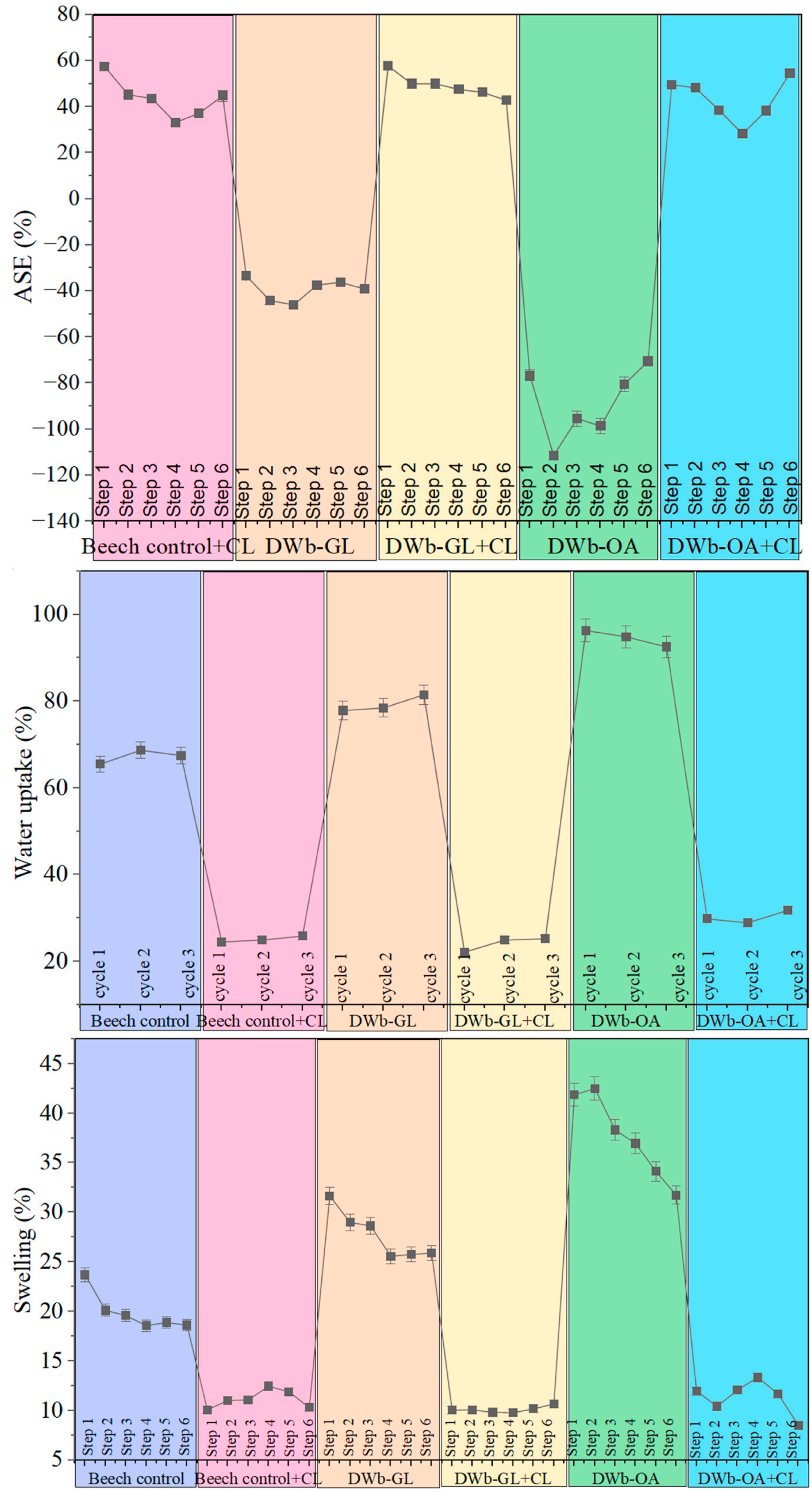

Fig. 4. Anti-swelling efficiency (ASE, %), Water uptake (%), and Swelling (%) of PCL modified Beech wood specimens.

67.44 %). This indicates that unmodified wood naturally absorbs high amounts of water and has low dimensional stability. Similarly, in the study by Ermeydan et al. [4], it was reported that for the reference pine uptake was close to 100 % and therefore it showed a high swelling tendency. In the Beech control + CL group, a significant decrease in water uptake rates was observed after CL modification (Cycle 1: 24.42 %; Cycle 3: 25.76 %). These results reveal that polycaprolactone reacts with the hydroxyl groups in the cell wall to form a water-resistant structure. As reported in the literature, water uptake drops below 50 %, especially in modifications performed in the 2–4 % catalyst range. In the DWb-GL group, specimens delignified with glycerol-based DES but were not treated with CL showed high levels of water uptake (Cycle 1: 77.85 %; Cycle 3: 81.50 %). This is related to the cell wall becoming more hydrophilic after lignin removal, and it has been reported in the literature that delignification alone can reduce dimensional stability. However, in the DWb-GL + CL group, subjected to the same DES treatment and subsequently modified with CL had water uptake rates ranging from 22 to 25 %. These values indicate that the modification was effective and that polycaprolactone could penetrate more easily into structures with reduced lignin content. Similarly, for the DWb-OA group, treated with only oxalic acid-based DES, very high water uptake rates (Cycle 1: 96.33 %; Cycle 3: 92.55 %) were observed. This suggests that the strong delignification effect weakens the structural integrity of the cell wall and leads to a loss of resistance to water. However, in the DWb-OA + CL treatment group, water uptake values after polycaprolactone application remained between 29.75 % and 31.73 %, a significant decrease compared to the control group. This demonstrates that the -OH groups exposed by DES were effectively modified by CL, preventing water penetration into the polymer structures. In our study, the polycaprolactone modification performed with 3 % catalyst significantly reduced water uptake rates in both unmodified and delignified beech. The DES + CL combination was particularly effective on lignin-reduced structures, consistent with the high-water repellency levels achieved in the 2–4 % catalyst range reported in the literature [2]; [4]. These findings provide strong evidence that CL enhances dimensional stability by integrating into wood cell walls via graft polymerization. Weight loss (%) values following water uptake tests for beech and pine wood samples are presented in Fig. S1. Additionally, ASE (%), swelling (%), and water uptake (%) for Scots pine (*Pinus sylvestris* L.) specimens are also included in Fig. S2. As similar trends were observed in the Scots pine specimens to the beech specimens, these findings are not included in the main text but are presented in the supplementary file.

Although the improvements in ASE, water uptake, and swelling values resulting from the combined application of DES pretreatment and ε-caprolactone modification may appear limited at first glance, these results should be evaluated considering the chemical mechanism of the process. Rather than directly increasing hydrophobicity, the DES treatment aims to increase the accessibility of reactive sites where ε-CL can graft by partially removing lignin from cell wall components and exposing hydroxyl groups. This allows ε-CL to penetrate more homogeneously and deeply into the wood structure. While this did not produce dramatic differences in short-term tests (ASE, water uptake, swelling), it did provide significant advantages in terms of chemical bonding depth, structural homogeneity, and long-term dimensional stability. Furthermore, FTIR and SEM analyses demonstrated that lignin removal and cell wall loosening occurred after DES treatment [31]. These structural changes support that ε-CL polymer chains reach the inner cell layers, creating a more durable and stable modification.

In Table S2–S4, different letters indicate statistically significant differences ($p < 0.05$). Statistical testing showed that there were significant differences between treatment groups ($p < 0.05$). DWb-OA + CL specimens had statistically lower ASE value, while DWb-OA specimens had the highest ASE for beech wood. While the pine specimens showed a similar trend, the lowest ASE was obtained in the DWp-GL specimens. Statistically, there was no significant difference in water uptake between DWb-GL + CL and Beech control + CL, and the lowest water uptake occurred in these sets. In pine specimens, Pine control + CL, DWp-GL + CL, and DWp-OA + CL showed the lowest water uptake values in the same homogeneity group.

3.3. Chemical structure of DES-treated and ε -caprolactone modified wood specimens

In Fig. 5, FTIR analysis results clearly demonstrate the effects of chemical modifications applied to beech wood specimens. The broad band observed in the spectrum of raw beech wood, between 3300 and 3400 cm^{-1}, represents the hydroxyl stretching vibration corresponding to –OH groups in cellulose and hemicellulose structures. Furthermore, C–H stretching vibrations around 2900 cm^{-1} indicate the presence of aliphatic structures within the lignocellulosic structure. The prominent peak in the 1730–1740 cm^{-1} region indicates carbonyl (C=O) groups originating from hemicellulose components. In the delignified DWb-OA and DWb-GL specimens, a decrease in aromatic ring vibrations, specific to lignin structure, was observed between 1510 and 1600 cm^{-1}. This indicates a decrease in lignin content and a successful delignification process. At the same time, an increase in C–O stretching vibrations in the 1000–1100 cm^{-1} region indicates that glycosidic bonds within the cellulose structure become more dominant, and these structures are more clearly detected in the spectra after lignin removal. In the specimens modified with **ε** -Caprolactone (Beech control + CL, DWb-OA + CL, and DWb-GL + CL), new and sharp carbonyl peaks were detected in the 1735–1750 cm^{-1} range. These peaks prove that **ε** -caprolactone reacts with hydroxyl groups and integrates into the structure via ester bonds. Modification-induced changes were particularly pronounced in the DWb-OA + CL and DWb-GL + CL variants, due to synergistic effects of lignin removal and caprolactone integration. These findings demonstrate that **ε** -caprolactone successfully interacted with the delignified wood matrix and introduced new functional groups.

The C=O/O–H peak ratios presented in Table 1 quantitatively indicate the degree of PCL grafting in the samples. While the ratio was approximately 1.0 in the control sample, it decreased to approximately 0.8 in the PCL modified samples. This decrease indicates that the hydroxyl groups reacted to form ester bonds and that PCL was successfully grafted onto the surface. Thus, FTIR analysis quantitatively confirmed that chemical modification had occurred and the material had acquired a more hydrophobic character. Additionally, the quantitative evaluation of Scots pine samples is included in Table S1.

DES are environmentally friendly solvents that have the potential to selectively separate the structural components of lignocellulosic biomass. Oxalic acid-glycerol or oxalic acid-cholesterol DESs, in particular, are notable for their ability to dissolve lignin fractions. Studies have already highlighted significant reductions in the intensity of aromatic bands specific to the lignin structure in DES-treated wood using spectral methods such as FTIR and NMR [33]; [28,34]. These findings indicate that the DES treatment solubilizes phenolic hydroxyl and aromatic moieties from lignin, thereby enriching the relative abundance of cellulose and hemicellulose in the residual wood matrix. Therefore, the observation that aromatic C=C vibrations in the 1500–1600 cm^{-1} range in the FTIR spectrum of DES pretreated and delignified beech (Fig. 5) and Scots pine specimens in our study (Fig. S3) is reduced, is consistent with the findings in the literature [28].

The modification process with polycaprolactone causes significant changes in the chemical structure of wood cell walls, potentially increasing the physical and biological durability of the material. PCL reacts with wood polymers having hydroxyl groups (especially cellulose and hemicellulose) via ring-opening polymerization, resulting in the formation of PCL chains that are covalently bonded to the cell wall [4]. As a result of this process, the carbonyl (C=O) group peaks characteristically observed in the 1720–1730 cm^{-1} region in FTIR analyses are the most obvious indicators confirming the presence of PCL [19]. In addition, wood specimens modified with ε-CL stand out with their high

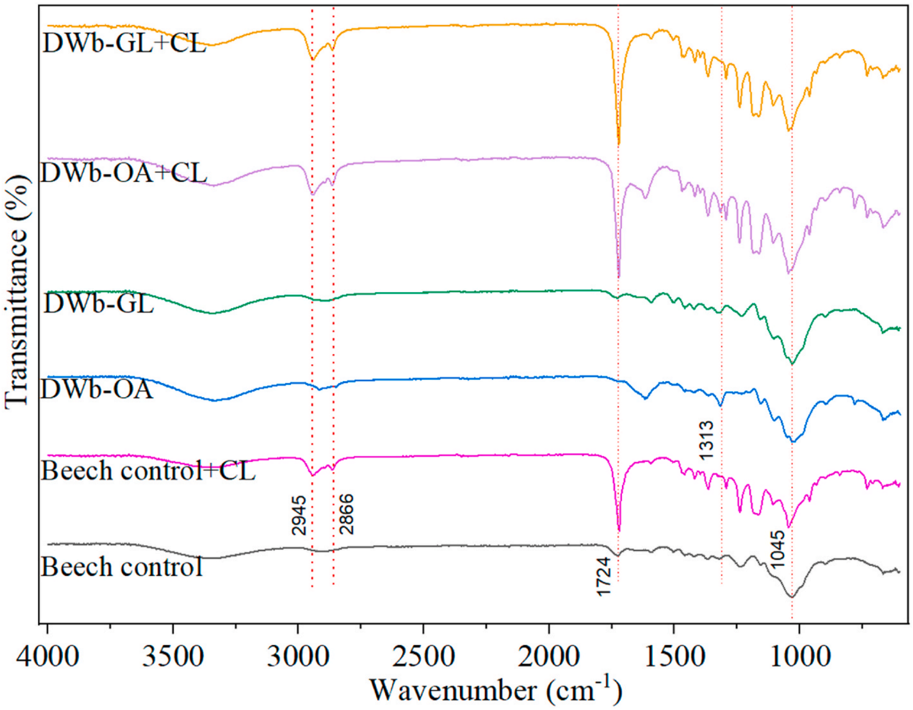

Fig. 5. FTIR spectra of beech control, DES pretreatment and PCL modified wood specimens.

Table 1
FTIR peak ratios (C=O/O–H) and quantitative evaluation of the PCL grafting process.

Samples	1730 cm^{-1} (C=O)	3400 cm^{-1} (O-H)	C=O/O-H rate
Beech control	95.88	94.67	1.01
Beech control + CL	81.72	94.67	0.86
DWb-OA	96.70	90.60	1.07
DWb-GL	96.19	91.07	1.06
DWb-OA + CL	72.31	89.40	0.81
DWb-GL + CL	71.12	91.83	0.77

anti-swelling efficiency (ASE) and low water uptake rates; showing that the modification imparts hydrophobic character and suppresses hygroscopic behavior [4] of wood. Similar trends, as reported for beech above, were observed in the Scots pine specimens and the FTIR spectra of Scots pine are therefore not included in the main text but presented in the supplementary file Fig. S3.

3.4. *Thermal behavior of delignified wood modified with ε -caprolactone*

Fig. 6 shows the TGA results of beech control, DES-treated, and CL-modified treatment sets. TGA results of Scots pine specimens are

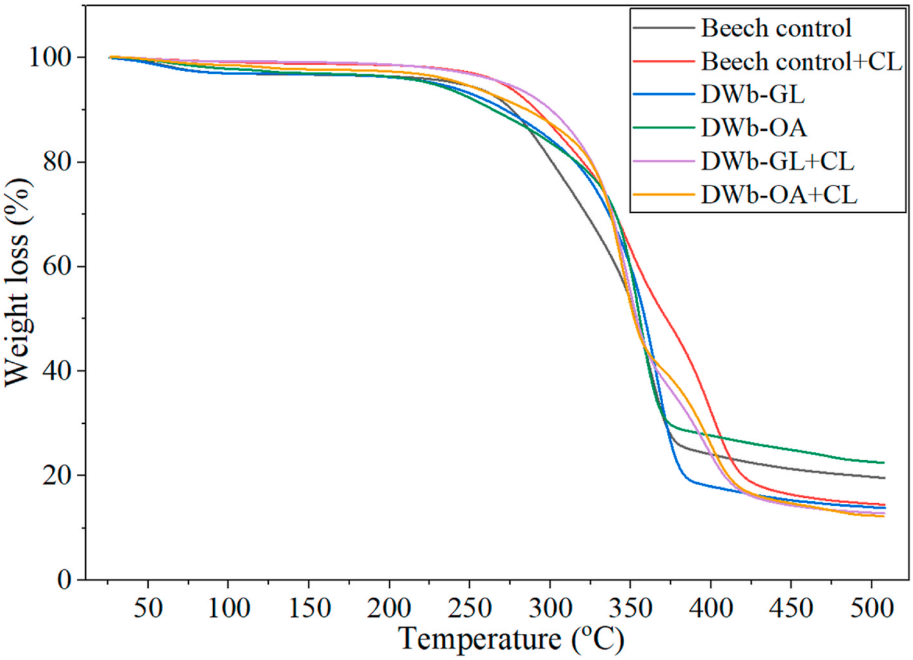

Fig. 6. TGA curves of beech control, DES pretreatment and PCL modified wood specimens.

presented in Fig. S4–S5. In the DES-treated specimens (DWb-OA and DWb-GL), a more rapid thermal degradation behavior was observed due to the removal of lignin. Notably, the onset of mass loss occurs at lower temperatures, particularly within the 100 °C–300 °C range. In contrast, the caprolactone (CL)-modified treatment sets exhibited higher resistance to thermal degradation up to 300 °C. However, after 500 °C, greater mass loss was observed for these sets compared to the control group. When the DTG curves for both beech and Scots pine (Fig. S4, Fig. S6) were examined, it was understood that the degradation in the CL-modified specimens occurred in two stages, resulting from the decomposition of polycaprolactone in addition to the wood components. Literature studies have reported that PCL has a two-stage degradation process and not a single degradation mechanism [35]. Considering the residue amounts, the DWb-OA specimen exhibited the highest charring rate at 22.45 %, while the DWb-GL and especially the variants combined with CL achieved the lowest residue values. These findings clearly demonstrate that the DES treatment reduces thermal stability of modified wood by reducing proportions of lignin from the wood matrix, while the CL modification, although increases thermal resistance at low temperatures; creates additional degradation mechanisms when modified wood is exposed to higher temperature ranges [36].

3.5. X-ray diffraction analysis of structurally modified wood materials

The XRD results of control, DES pretreated wood (DW) wood, and the PCL modified wood are presented in Fig. 7 for beech and Fig. S7 for Scots pine wood.

XRD analyses of beech wood control specimens, DWb-GL and DWb-OA delignified specimens and their PCL modified variants reveal the impact of chemical modifications carried out in the lignocellulosic matrix on cellulose crystallinity. Delignification caused a significant increase in the crystalline peak intensity (2θ ≈ 22.5°) and a decrease in the amorphous lignin and hemicellulose region intensity (2θ ≈ 18°) in DWb-GL and DWb-OA specimens (002) (~26 % and ~27 %, respectively) compared to the control. As a result of XRD analyses, crystallinity values indices (CrI, %) were calculated using the Segal peak height method [30]. According to the CrI values obtained, Beech control specimens showed 45.58 % crystallinity, which decreased to 35.89 % after ε-CL grafting. This indicates successful CL grafting and partial disruption of the crystalline regions by increasing the amorphous structure. A similar pattern was observed in the DWb-GL group. While the crystallinity value was found to be quite high at 55.54 % in specimens delignified with glycerol-based DES, this value decreased to 45.42 % in the DWb-GL + CL specimens modified with CL. The same trend was observed in the DWb-OA and DWb-OA + CL sets. While the crystallinity values in the wood specimens treated with oxalic acid-based DES was 54.33 %, it decreased to 45.23 % after CL modification.

These results indicate that DES treatments contribute to a more ordered cellulosic structure (i.e., increased crystallinity values) by partially dissolving and removing lignin. However, the subsequent CL modification causes some of the crystalline regions to be disrupted because the polymer settles into the cell wall, creating a partially amorphous structure. This observation is of particular importance as it demonstrates that CL was successfully integrated into the structure through graft polymerization and that the modification induced desired structural changes in wood.

Fig. S5 shows the XRD results of Scots pine. These results indicate that modifications and pretreatments exhibited crystallinity values trends similar to those in beech samples. DES treatments (especially GL- and OA-based ones) increased the crystallinity values by solubilizing lignin; the subsequent PCL modification caused a partial decrease in crystallinity values due to the integration of the polymer into this structure. Specifically, the increase in CrI in the control + CL group (35.77 % → 39.28 %) indicates that CL was successfully grafted onto the lower lignin-containing structure and interacted with the cellulosic matrix. This trend is consistent with structural changes previously observed and reported for beech samples.

The macroscopic performance of the changed wood may be directly linked to the partial drop in the CrI values following ε-CL grafting, in addition to the observed changes in crystallinity values. The decrease in crystallinity values suggests that the PCL chains broke through the hydrogen-bonded crystalline network and entered the ordered cellulose areas, creating a more amorphous structure. This enhanced amorphous nature improves interfacial adaptation and ductility by increasing chain mobility and flexibility inside the cell wall matrix. Additionally, adding hydrophobic PCL segments improves the wood's dimensional stability

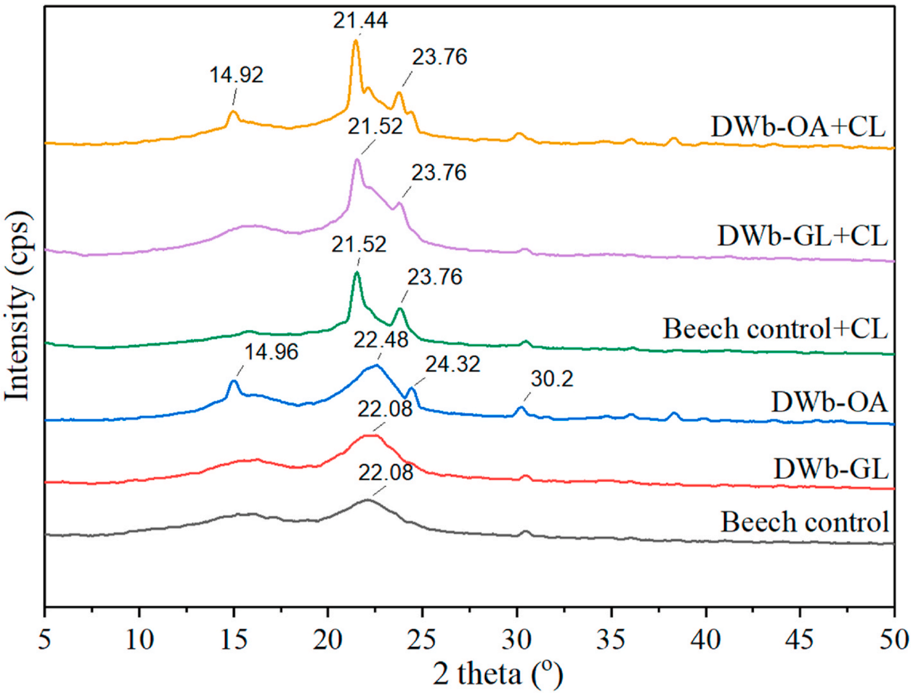

Fig. 7. XRD results of control, DES pretreatment and PCL modified wood specimens.

and water resistance by lowering its surface polarity. Consequently, the decrease in crystallinity values is a beneficial structural change that gives the PCL-modified specimens more flexibility and hydrophobicity rather than a degrading effect.

In a previous study, attempts were made to evaluate the effect of DES treatment on the crystalline structure of wood. In this study, the XRD patterns of natural wood and specimens impregnated with DES and then oven-dried were compared, and similar peaks were detected in both groups at $2\theta = 16.2^\circ$ (101), 22.5° (002), and 34.7° (040), which are the characteristic diffraction peaks of the cellulose I polymorph [37]. These similarities indicate that the DES treatment does not significantly change the crystalline structure of cellulose. However, the study reported that the crystallinity index (CrI) in DES-treated wood increased significantly compared to natural wood (35.66 %), which according to the authors, were due to the partial removal of hemicellulose, lignin, and amorphous portions of cellulose during post-treatment ethanol washing [37]. These findings are similar to the CrI increases observed in the DES-treated beech and Scots pine in our study and are consistent with our assessment that DES relatively increases the crystalline regions of cellulose by reducing the amorphous components.

4. Conclusion

In this study, the selective removal of lignin from the wood cell wall using DES and subsequent modification of the lignin-reduced structure with ε- CL via in situ polymerization were successfully achieved. By selectively removing lignin and enhancing hydroxyl group accessibility, DES pretreatment facilitated deeper penetration and more uniform grafting of polycaprolactone chains within the wood matrix. It further enhanced the effectiveness of ε-CL modification, providing more homogeneous bonding in the wood structure, yielding enhanced moisture resistance and long-term dimensional stability, thus demonstrating an in-depth modification impact beyond superficial changes.

FTIR analysis confirmed successful ε- CL binding to the wood cell wall through the presence of ester carbonyl bands near 1720 cm^{-1}, alongside a noticeable reduction in lignin-associated peaks following DES treatment. XRD results revealed a marked decrease in crystallinity, indicating a shift toward a more amorphous wood structure. Complementary TGA data further validated the enhancement in thermal stability, collectively demonstrating the synergistic impact of the combined DES–CL modification. This synergistic strategy has demonstrated positive outcomes across both coniferous and hardwood species, underscoring its potential as a versatile approach for advancing the functional performance of wood-based materials in future applications.

This integrated approach opens new pathways for developing high-performance, bio-based materials, reinforcing wood's role as a sustainable alternative in modern material science. Future work should systematically investigate the physical and mechanical performance of wood specimens subjected to more extensive lignin removal and impregnated with lower caprolactone loadings, in order to identify optimal treatment parameters for enhanced material properties. Also, solid state NMR analyses are recommended to verify the degree of covalent bonding of ε-caprolactone with wood polymers and whether the polymerization has occurred completely.

CRediT authorship contribution statement

Şeyma Özlüsoylu: Resources, Methodology, Investigation. **Ahmet Can:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Sauradipta Ganguly:** Writing – review & editing, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank the Natural Resources Institute, Finland (LUKE) for the support in preparing this paper, and the Regional council of North Karelia for allowing co-funding from European Union, Just Transfer Fund through PUHTIA KEH project (funding decision 2021/901403/09 02 01 01/2023/PKARJALA).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2025.109061.

Data availability

Data will be made available on request.

References

[1] M. Cambazoglu, E.D. Tomak, M.A. Ermeydan, Natural weathering of spruce wood chemically modified by re-used ε-caprolactone solution, Color. Technol. 139 (3) (2023) 265–275.

[2] M.A. Ermeydan, E. Cabane, P. Hass, J. Koetz, I. Burgert, Fully biodegradable modification of wood for improvement of dimensional stability and water absorption properties by poly (ε-caprolactone) grafting into the cell walls, Green Chem. 16 (6) (2014) 3313–3321.

[3] R. Li, Z. Zhang, G. Liu, X. Han, J. Pu, Inserting poly (ε-caprolactone) into wood cell wall structures for dehydration and consolidation of waterlogged Scots pine wood, Bioresources 13 (1) (2018) 881–893.

[4] M.A. Ermeydan, M. Cambazoğlu, E.D. Tomak, A methodological approach to ε-caprolactone modification of wood, J. Wood Chem. Technol. 42 (4) (2022) 286–296.

[5] S. Ganguly, S.K. Hom, A.K. Sethy, S. Dan, B. Debnath, V. Sharma, S. Tripathi, D. Kržišnik, M. Petrič, Impact of microwave irradiation pretreatment on preservative retention and durability of outdoor-exposed Norway spruce, Results Mater. (2025) 100807, https://doi.org/10.1016/j.rinma.2025.100807.

[6] R.M. Rowell, Chemical modification of wood: a short review, Wood Mater. Sci. Eng. 1 (1) (2006) 29–33, https://doi.org/10.1080/17480270600670923.

[7] R.M. Rowell, Understanding wood surface chemistry and approaches to modification: a review, Polymers 13 (15) (2021) 2558, https://doi.org/10.3390/polym13152558.

[8] E.D. Tomak, A. Can, M.A. Ermeydan, Biodegradability of poly (Ɛ-Caprolactone) modified wood by decaying fungi, J. Polym. Environ. 31 (9) (2023) 4097–4111.

[9] M.G. Morán-Aguilar, I. Costa-Trigo, A.M. Ramírez-Pérez, E. de Blas, M. Calderón-Santoyo, M.G. Aguilar-Uscanga, J.M. Domínguez, Development of sustainable biorefinery processes applying deep eutectic solvents to agrofood wastes, Energies 15 (2022) 4101.

[10] X.L. Zhou, T.J. Huang, J. Liu, H.L. Gao, H.Y. Bian, R.B. Wang, C. Huang, J.L. Sha, H.Q. Dai, Recyclable deep eutectic solvent coupling sodium hydroxide post-treatment for boosting woody/herbaceous biomass conversion at mild condition, Bioresour. Technol. 320 (2021) 124327.

[11] Y. Shen, B. Fan, Y. Xin, Q. Zhou, Y. Wang, H. Zhou, H. Gao, Ternary deep eutectic solvent-mediated rapid extraction of highly crystalline cellulose enabling closed-pore regeneration of hard carbon anode for ultrafast sodium storage, Carbon 243 (2025) 120594.

[12] C. Huang, J. Cheng, Y. Zhan, X. Liu, J. Wang, Y. Wang, X. Song, Utilization of guaiacol-based deep eutectic solvent for achieving a sustainable biorefinery, Bioresour. Technol. 362 (2022) 127771.

[13] X. Liu, J. Cheng, C. Huang, J. Wang, G. Fang, K. Shen, A.J. Ragauskas, Alkali-facilitated deep eutectic solvent for effective bamboo saccharification, Bioresour. Technol. 367 (2023) 128297.

[14] L. Yao, P. Cui, X. Chen, C.G. Yoo, Q. Liu, X. Meng, H. Yang, A combination of deep eutectic solvent and ethanol pretreatment for synergistic delignification and enhanced enzymatic hydrolysis for biorefinary process, Bioresour. Technol. 350 (2022) 126885.

[15] V. Ippolitov, I. Anugwom, R. van Deun, M. Mänttäri, M. Kallioinen-Mänttäri, Cellulose membranes in the treatment of spent deep eutectic solvent used in the recovery of lignin from lignocellulosic biomass, Membranes 12 (1) (2022) 86.

[16] R. Ma, Q. Zhang, S. Wang, B. Li, L. Ma, L. Zhang, Z. Wang, One-pot cellulose nanofibrillation, surface-modification and grafting by deep eutectic solvent towards high performance 3D printing nanocellulose-enriched bionanocomposites, Ind. Crop. Prod. 210 (2024) 118134.

[17] Y. Huang, K. Jiang, Y. He, J. Hu, K. Dyer, S. Chen, B.B. Xu, A natural lignification inspired Super-Hard wood-based composites with extreme resilience, Adv. Mater. 37 (19) (2025) 2502266.

[18] M.A. Ermeydan, Z.N. Kartal, E.D. Tomak, Effect of process variations of polycaprolactone modification on wood durability, dimensional stability and boron leaching, Holzforschung 73 (9) (2019) 847–858.

[19] M.A. Ermeydan, M. Babacan, E.D. Tomak, Poly (ε-caprolactone) grafting into Scots pine wood: improvement on the dimensional stability, weathering and decay resistance, Cellulose 28 (9) (2021) 5827–5841.

[20] J.T. Wiltshire, G.G. Qiao, Degradable core cross-linked star polymers via ring-opening polymerization, Macromolecules 39 (13) (2006) 4282–4285.

[21] M. Labet, W. Thielemans, Improving the reproducibility of chemical reactions on the surface of cellulose nanocrystals: ROP of ε-caprolactone as a case study, Cellulose 18 (3) (2011) 607–617.

[22] R. Kusumi, Y. Teramoto, Y. Nishio, Structural characterization of poly(e-caprolactone)-Grafted cellulose acetate and butyrate by solid-state 13CNMR, dynamic mechanical, and dielectric relaxation analyses, Polymer (Guildf.) 52 (2011) 5912–5921, https://doi.org/10.1016/j.polymer.2011.10.032.

[23] M.T. Gustavsson, P.V. Persson, T. Iversen, K. Hult, M. Martinelle, Polyester coating of cellulose fiber surfaces catalyzed by a cellulose-binding Module- Candida Antarctica lipase B fusion protein, Biomacromolecules 5 (2004) 106–112, https://doi.org/10.1021/bm034244y.

[24] C. Bruce, C. Nilsson, E. Malmström, L. Fogelström, Paper-sheet biocomposites based on wood pulp grafted with poly (ε-caprolactone), J. Appl. Polym. Sci. 132 (23) (2015).

[25] C.F. Bellani, E. Pollet, A. Hebraud, F.V. Pereira, G. Schlatter, L. Avérous, M. C. Branciforti, Morphological, thermal, and mechanical properties of poly (ε-caprolactone)/poly (ε-caprolactone)-grafted-cellulose nanocrystals mats produced by electrospinning, J. Appl. Polym. Sci. 133 (21) (2016).

[26] S.C. Cintra, N.F. Braga, G.F.D.M. Morgado, T.L.D.A. Montanheiro, J. Marini, F. R. Passador, L.S. Montagna, Development of new biodegradable composites materials from polycaprolactone and wood flour, Wood Mater. Sci. Eng. 17 (6) (2022) 586–597.

[27] D. Smink, A. Juan, B. Schuur, S.R. Kersten, Understanding the role of choline chloride in deep eutectic solvents used for biomass delignification, Ind. Eng. Chem. Res. 58 (36) (2019) 16348–16357.

[28] A.E. Çelik, A. Can, Surface characterization of wood treated with acidic deep eutectic solvents, Eur. J. Wood Wood Prod. 81 (1) (2023) 143–157.

[29] A. Can, H. Sivrikaya, Removal of copper, chromium, and arsenic from CCA-treated wood using glycerol/choline chloride deep eutectic solvent, Environmental Sciences Proceedings 22 (1) (2022) 1.

[30] L.G.J.M.A. Segal, J.J. Creely, A.E. Martin Jr, C.M. Conrad, An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer, Textil. Res. J. 29 (10) (1959) 786–794.

[31] P. Li, C. Yang, Z. Jiang, Y. Jin, W. Wu, Lignocellulose pretreatment by deep eutectic solvents and related technologies: a review, J. Bioresour. Bioprod. 8 (1) (2023) 33–44.

[32] Z. Pei, X. Liu, J. Chen, H. Wang, H. Li, Research progress on lignin depolymerization strategies: a review, Polymers 16 (17) (2024) 2388.

[33] E.O. Owhe, N. Kumar, J.G. Lynam, Lignin extraction from waste biomass with deep eutectic solvents: molecular weight and heating value, Biocatal. Agric. Biotechnol. 32 (2021) 101949.

[34] M. Zhou, O.A. Fakayode, A.E.A. Yagoub, Q. Ji, C. Zhou, Lignin fractionation from lignocellulosic biomass using deep eutectic solvents and its valorization, Renew. Sustain. Energy Rev. 156 (2022) 111986.

[35] O. Persenaire, M. Alexandre, P. Degée, P. Dubois, Mechanisms and kinetics of thermal degradation of poly (ε-caprolactone), Biomacromolecules 2 (1) (2001) 288–294.

[36] A. Can, İ. Özlüsoylu, P. Antov, S.H. Lee, Choline chloride-based deep eutectic solvent-treated wood, Forests 14 (3) (2023) 569.

[37] A.M. Gondaliya, M. Hoque, S. Raghunath, E.J. Foster, Green and sustainable fabrication of DES-pretreated high-strength densified wood, Wood Sci. Technol. 58 (5) (2024) 1901–1923.