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CHEMICAL MODIFICATION OF PAULOWNIA, POPLAR, AND EUCALYPTUS WOOD BY ε-CAPROLACTONE GRAFTING INSIDE CELL WALLS TO IMPROVE WOOD PROPERTIES

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Abstract- Wood is an excellent engineering material with its light weight and high mechanical properties, and has been used for furniture production from the early ages of humankind. However, its susceptibility to biodegradation due to its hygroscopic nature and chemical composition limits usage of wood as outdoor furniture. For the outdoor utilization, chemical modification methods may provide long service-life to the products. Water repellence and dimensional stability can be both improved up to 70% and 40% respectively by inserting hydrophobic molecules inside spruce wood cell walls. Paulownia, Poplar, and Eucalyptus are fast growing trees and their wood has different properties. In this study, a pretty new modification method was carried out by grafting a hydrophobic polymer poly(ε-caprolactone) (PCL) onto economically valuable Paulownia, Poplar, and Eucalyptus wood cell walls. The water absorption, dimensional stability (ASE), equilibrium moisture content (EMC), and density change of poly(ε-caprolactone) grafted wood were characterized and found that dimensional stability and water repellence has significantly better compared to references for poplar wood but not for the paulownia and eucalptus.

Key Words- poli(ε-caprolacton), wood, chemical modification, dimensional stability.

PAVLONYA, KAVAK VE ÖKALİPTUS AHŞABININ ÖZELLİKLERİNİN İYİLEŞTİRİLMESİ İÇİN ε-KAPROLAKTON İLE KİMYASAL MODİFİKASYONU

Özet- Ahşap düşük özgül ağırlığına karşın yüksek direnç özelliklerine sahip olması nedeniyle mükemmel bir mühendislik malzemesidir ve insanlığın erken çağlarından bu yana mobilya üretiminde kullanılmaktadır. Bununla birlikte, biyolojik bozunmaya duyarlılığı, higroskopik yapısı ve kimyasal bileşiminden dolayı dış ortam mobilyalarında kullanımı kısıtlıdır. Dış mekanda kullanım için kimyasal modifikasyon metotları ürünlere uzun servis ömrü sağlayabilir. Ladin odun hücre duvarlarına hidrofobik moleküller yerleştirerek su iticiliği ve boyutsal kararlılığı sırasıyla %70 ve

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%40 oranında arttırılabilir. Pavlonya, Kavak ve Ökaliptus hızlı büyüyen ağaçlardır ve ahşapları farklı özelliklere sahiptir. Bu çalışmada ekonomik olarak değeri olan Pavlonya, Kavak ve Ökaliptus ahşap hücre çeperlerine hidrofobik bir polimer olan poli(ε-kaprolakton) (PCL) aşılanmasıyla çok yeni bir modifikasyon yöntemi uygulanmıştır Poli (ε-kaprolakton) aşılanmış farklı ahşap türlerinin su emme, boyutsal kararlılığı (ASE), denge rutubet miktarı (DRM) ve yoğunluk değişimi karakterize edildi. Kavak ahşabının özelliklerinin yüksek oranda iyileşmiş ancak pavlonya ve okaliptüste iyileşme görülmemiştir.

Anahtar Kelimeler- poli(ε-kaprolakton), ahşap, kimyasal modifikasyon, boyutsal stabilite.

1. INTRODUCTION

Wood is such an engineering material which has several advantages among other building materials. Having excellent mechanical properties with its light weight, being a renewable raw material, having process ability, aesthetic appearance, and sustainability are some of its advantages [1-3].

However, wood has also has some negative properties which limits its long-term utilization.
Due to its hygroscopic and hydrophilic structure, wood cell walls may absorb huge amount of water or moisture from the environment [4]. The water absorption and desorption cycles of wood is a powerful mechanical movement and swelling and shrinking of wood consequently cause dimensional instability, deformation and cracks on wood material [1-3].

Durability of wood is another disadvantage of wood which may boost by presence of water or high humidity in wood. Up to now wood modification research mainly focused on to improve decay resistance of wood. There are also some modification methods which also improves wood dimensional stability [5]. Dimensional stability and other wood properties can be improved by inserting chemicals inside wood cell walls and fixing them somehow to eliminate leaching problem [2,3,6]. Anhydrides, chlorides, cyanates, etc. can form covalent bonds with cell wall polymers [7,8]. Another chemical modification approach is in-situ polymerization of various monomers by either grafting them or by filling the cell wall voids with homopolymers [2,3,9-13]. However due to hydrophilic structure of wood cell wall it is difficult or almost impossible to insert conventional hydrophobic monomers inside cell walls for further polymerization reactions. Still, due to advantages of hydrophobic polymers against water absorption of materials, in-situ polymerization of hydrophobic monomers inside wood has been studied several times. There are a few number of successful studies reported recently which reports in-situ polymerization of hydrophobic monomer with an efficient and stable improvement of dimensional stability [11-14]. In one of those studies [12], it was reported for the first time that Norway spruce wood was modified in one step by in-situ graft polymerization of hydrophobic ε-caprolactone monomer. It was also reported that several wood properties were improved considerably without losing any mechanical strength of wood. By this method Ermeydan achieved to reduce equilibrium moisture content (EMC) about 30% and found an anti-swelling efficiency (ASE) about 40% [12,15,16]. Another advantage of this modification is the recycling problem which poly(ε-caprolactone) is one of the polymers that can be consumed by bio-organisms[17].

In this study, different type of wood: paulownia (*Paulownia* spp.), poplar (*Populus tremula* L.), and eucalyptus (*Eucalyptus camaldulensis* Dehn. (Turkish river red gum)) which are all from angiosperm trees, were used instead Norway spruce and pine that was used in the previous studies [12,15,16]. Our aim was to investigate potential of the poly(ε-caprolactone) (PCL) modification in different types of hardwood species for the first time. Hydrophobic ε-caprolactone monomer was successfully grafted into the wood cell walls of poplar wood, but not to eucalyptus and paulownia wood. In this study it was observed that PCL has a potential to modify poplar wood in terms of dimensional stability (40% ASE) and water repellence (40%).

2. METHODS

Materials: ε-caprolactone (CL), pyridine, tin(II) octoate (Sn(oct)$_2$), acetone, dimethyl formamide (DMF) were bought from SiAl and used as received.

2.1. Sampling of wood: Twenty paulownia, poplar, and eucalyptus sapwood sample (1 cm x 0,5 cm x 1 cm; radial x tangential x longitudinal) for each species were cut along the grain, and dried at 63°C over night. The samples were divided in two sets: 10 samples as reference (i.e. untreated), 10 samples as modification (poly(ε-caprolactone) grafted). After modification step, 5 samples from each set were used to make water uptake (WU), leaching, swelling (S), anti-swelling efficiency (ASE) tests, 5 were used to make equilibrium moisture content (EMC) test.

2.2. Impregnation and grafting polymerization of ε-caprolactone: Samples from each wood species separately put into round bottom flask. Samples for modification were immersed into DMF for overnight for swelling. A solution of 20g ε-caprolactone with 0,8 g initiator Sn(Oct)$_2$ were rinsed onto wood samples and samples were kept in the overnight to increase impregnation of monomer into cell walls before polymerization reaction. On the other day, dry DMF (20ml) were poured into the reaction media and nitrogen was used to degas reaction solution by bubbling for 10 min. Polymerization was carried out at 105°C (overnight). Reaction was completed by starting acetone washing with many portions of acetone for 4 hours, and then with distilled water (overnight). At the end, wood samples were dried at 63°C (overnight). DMF and acetone which were used for polymerization and washing process are good enough for dissolving both polycaprolactone and ε-caprolactone monomer. Pictures of the untreated and modified samples are shown in Figure1.

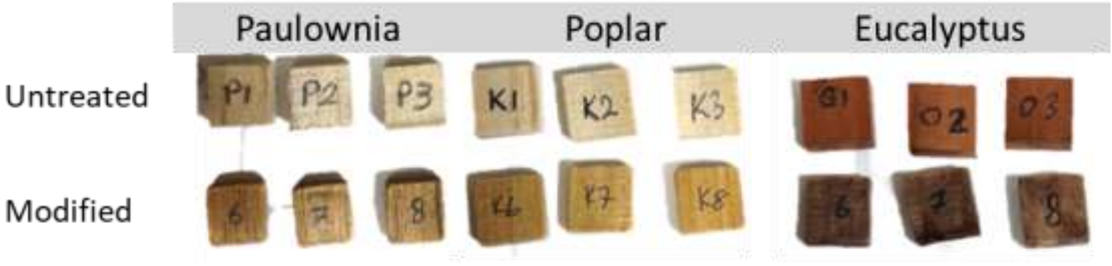
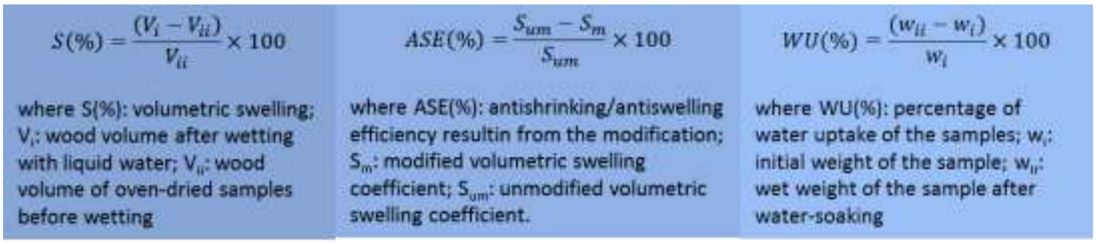


Figure 1. Photographic illustration of untreated and modified wood samples of paulownia, poplar, and eucalyptus wood.

Material Characterization

2.3. Weight Percentage Gain (WPG) and Volume Changes: To find out weight caused by the chemical treatment, weights and dimensions of the wood samples were measured before and after each treatment (caprolactone polymerization, water immersion, and oven drying).



$$S(\%) = \frac{(V_i - V_{ii})}{V_{ii}} \times 100$$

where S(%): volumetric swelling; V_i: wood volume after wetting with liquid water; V_{ii}: wood volume of oven-dried samples before wetting

$$ASE(\%) = \frac{S_{um} - S_m}{S_{um}} \times 100$$

where ASE(%): antishrinking/antiswelling efficiency resultin from the modification; S_m: modified volumetric swelling coefficient; S_{um}: unmodified volumetric swelling coefficient.

$$WU(\%) = \frac{(w_{ii} - w_i)}{w_i} \times 100$$

where WU(%): percentage of water uptake of the samples; w_i: initial weight of the sample; w_{ii}: wet weight of the sample after water-soaking

Figure 2. Equations of Swelling (S), Antiswelling efficiency(ASE), Water Uptake (WU).

2.4. Water Uptake (WU), Mass Loss, Swelling Coefficient (S), and Anti-Swelling Efficiency (ASE): The modified paulownia, poplar, and eucalyptus wood with their reference samples were soaked into distillated water for five days with a fair shaking (Soak cycle 1). Then samples were dried into an oven at 103°C over night (Drying cycle 1). Samples were soaked again into distilled water for the second water-soaking and drying cycles. The dimensional stability of the modified wood samples was obtained by calculating the S and the ASE values as reported [18]. The equations for swelling, anti-swelling efficiency, and WU calculations are given in Figure 2. The water repellence ability of modified wood is described by the WU calculations.

2.5. Equilibrium Moisture Content (EMC): 5 modified and 5 reference wood samples for each species were put into 35% humidity at room temperature in a closed chamber. Samples were weighted until they have stable weight which means saturated by humidity at given conditions. Weight of the samples were recorded, and then dried at 103°C overnight. Dry weight of samples also recorded. EMC were calculated as = 100 x (Wet weight-Dry weight)/ Dry weight.

3. FINDINGS

3.1. Weight Percentage Gain%:

Table 1. Weight percentage gain after ring opening polymerization reactions.

	Pawlonia	Poplar	Eucaliptus
WPG %	2,41	14,94	6,23

Percentage weight gain of wood samples after modification is a first indication of the success of modification process.

3.2. Dimensional Stability of Modified Samples:

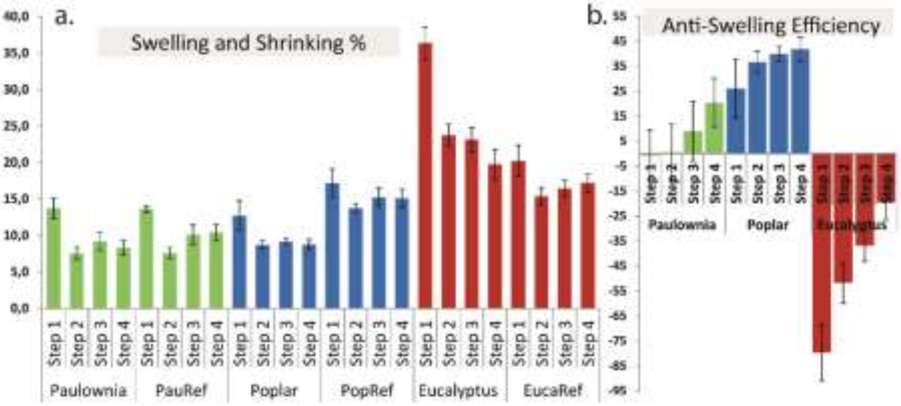


Figure 3. Swelling and Anti-Swelling Efficiency Values of Paulownia, Poplar, and Eucalyptus wood.

Dimensional stability of modified samples can be analyzed with anti-swelling efficiency calculations. Equation for calculation of anti-swelling efficiency (ASE%) is given in Figure 2. ASE gives us how much have the modified samples better dimensional stability in percentage.

3.3. Moisture/Water Uptake and Material Release of Modified Samples:

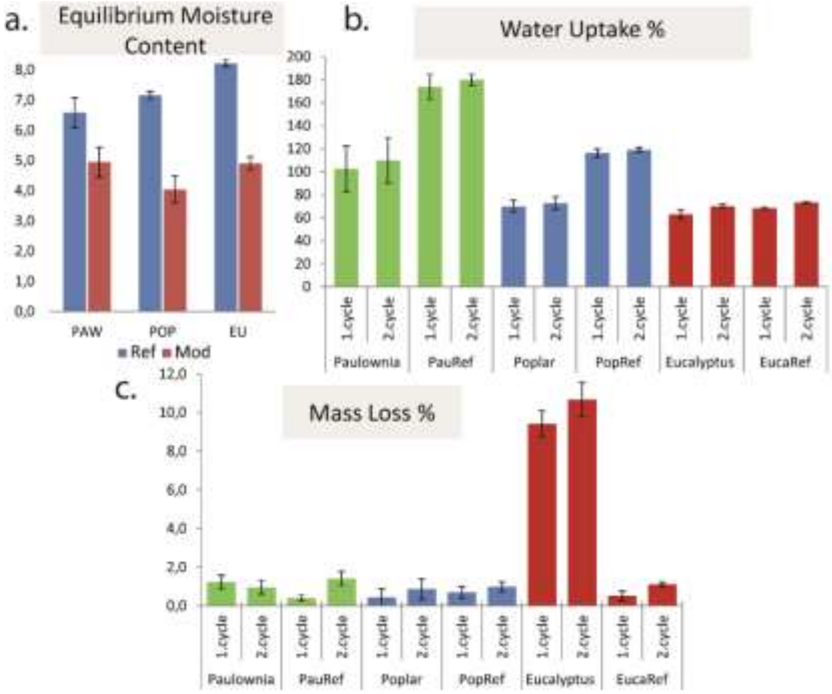


Figure 3. Equilibrium Moisture Content, Water Uptake, and Mass Loss of the Paulownia, Poplar and Eucalyptus wood, and their comparison with references.

Equilibrium moisture content% shows the capacity of humidity uptake of the samples. Mechanism of moisture uptake and water uptake is different. So, water uptake% capacity of the modified and reference samples also found. Mass loss% calculations indicates stability of the modification in some way that during leaching process how much material is washed out can be found. Thus, effect of modification process on wood also can be interpreted.

4. CONCULUSION AND DISCUSSION

4.1. Polycaprolactone Grafting onto Wood: ε-caprolactone can be polymerized to obtain poly(ε-caprolactone) by ring-opening polymerization (ROP), generally catalyzed with metal based catalysts (aluminum and tin based catalysts, alkaline earth metals, transition metals, and rare earth metals) [19,20], additionally organic catalytic or enzymatic systems [21,22]. Hydroxyl groups in the polymerization media can proceed as co-initiators for the polymerization by forming stannous alkoxide.

Cellulose hydroxyl groups were already studied as initiators for the ring-opening polymerization of ε-caprolactone and PCL grafted cellulose has been synthesized several times [23-26]. Use of caprolactone polymerization into wood is rather a novel approach and has been studied a few times so far [12,15,16]. In all of the early studies softwood was used such as pine. In our study hardwood of three species, paulownia, poplar and eucalyptus were used to start polymerization of ε-caprolactone. ε-caprolactone immersion in the cell wall structure is a difficult task because of the hydrophobicity of caprolactone monomer and cell wall structure. It was thought that the only issue is hydrophobicity, but in this study we observed that especially with hardwood, there may be various consequences of ε-caprolactone polymerization with different type of wood.

The weight percentage gain (WPG %) was measured and calculated after PCL synthesis help us to understand the success of the modification. The highest WPG% after polymer modification belongs to poplar samples (Table 1). Poplar has about 15% WPG, where paulownia and eucalyptus have 2,4% and 6,2%, respectively. This is probably due to the chemical and cell wall structure of wood cell walls. In fact, for poplar and paulownia, higher WPG is expected because they are known as highly porous woods with about 0,4 and 0,3g/cm^3 respectively. Problem of WPG% of paulownia can be the quality and age of wood which means paulownia wood used in this study was cut almost 20 years ago, thus wood itself already overdried in years and deformed a lot as it was observed during modification process, several wood particles was seen in the reaction media after polymerization. From our lab experience, it can be said that modification is better working with fresh samples. For the eucalyptus wood, there is again a low WPG% which might be due to the extractives in the cell walls and high density. Besides, eucalyptus wood is already known as a wood that is difficult to make conventional impregnation [27].

4.2. Dimensional Stability of Modified Wood: To evaluate the changes of dimensional stability of after modification of wood species, swelling and shrinkage of the wood samples during water soaking–drying cycles were investigated. The volumetric S values of the polymer grafted samples were compared with the reference (unmodified) after each water-soaking and drying cycle (Figure 3a). The reference paulownia, poplar and eucalyptus wood typically swells 10%, 15%, 18%, respectively. After polymer material fills the cell wall, less water can penetrate into the cell wall, thus modified wood should be less swell or shrink. Swelling and shrinking values of poplar reduced considerably (15% to 8%) and paulownia slightly (10% to 8%), however S values of eucalyptus increased up to 23% after modification (Figure 3a). Lower swelling means higher dimensional stability. In Figure 3b, ASE% values are given which compares the swelling of unmodified wood with the swelling of modified wood. Related formulation fo ASE% is shown in Figure 2. High ASE% corresponds to high dimensional stability. Poplar has the highest ASE% values against poplar reference up to 42% where paulownia has an increasing ASE% up to 20%. The increasing ASE% can be explained by the re-arrangement of polymer in the cell wall and better fixation of polymer to limit swelling and shrinking. However, eucalyptus has negative ASE% which may be explained by the removal of extractives or change of extractive chemistry to be better leached out with solvents and besides, negative ASE means that there is almost no polymer in the wood cell walls, but in the lumen.

4.3. Mass Loss and Water Repellence of Modified Wood: To investigate how does the modification effect on water repellence of wood, EMC test was carried out in the first place. The samples were put in a closed chamber at room temperature (22 °C) and a relative humidity of 35%. Under these conditions, reference (unmodified) reference paulownia, poplar and eucalyptus wood has an EMC of about 6,6%, 7,1%, 8,2% respectively (Figure 3a). Polycaprolactone grafted wood samples have less moisture content for all three species (5%, 4%, 4,9%) which corresponds 23%, 43%, 40% reduction of moisture uptake respectively. The highest reduction of EMC after modification belongs to poplar wood, than eucalyptus and paulownia.

The water uptake may have different mechanism than moisture uptake. After five days in water (1st cycle), the reference paulownia, poplar and eucalyptus wood samples gains about 180%, 120%, 70% water respectively, while wood modified with polycaprolactone gain 105%, 70%, 65% respectively (Figure 3b). Those results correspond to 33%, 42%, 7% reduction of water uptake for paulownia, poplar, and eucalyptus wood respectively. This trend is not very similar to moisture uptake results for paulownia and eucalyptus but poplar. It can be said that the grafted hydrophobic poly(caprolactone) provide some degree of water repellence for paulownia, and the best case is poplar. However, water uptake of eucalyptus is not getting better considerably.

Water immersion and oven drying cycles inevitably create mass loses of wood because of leaching of extractive and un-bound polymeric materials after modification. The mass losses recorded for the different samples are given in Figure 3c. For almost all samples of there is an acceptable mass losses during immersion-drying cycles, only about 1-2%. However, for modified eucalyptus wood lost totally 20% of mass. This may be explained that the extractives of eucalyptus may be modified also and removal of those materials is getting easier due to that chemistry change.

4.4. Conclusion:

Here, three hardwood species were modified with polycaprolactone polymerization for the first time at 105°C. ε-caprolactone were polymerized to increase properties of wood. Especially poplar wood has considerable improvement both for dimensional stability and water repellence with a 14% WPG. Paulownia has also improved dimensional stability to some extent, but eucalyptus wood is not convenient for such modification probably due to its high extractive content and chemistry. This method and new materials may be an alternative to expensive wood species because poplar is known as a fast growing tree and 40% of quality improvement will be very advantages. Besides, polycaprolactone is biodegradable, thus there will be no disposal problem of material after its lifetime.

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