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Improvement of mechanical, dimensional and biological stability of woods via gamma-radiation by using allyl alcohol-based copolymers

Odunların mekanik, boyutsal ve biyolojik kararlılığının allil alkol esaslı kopolimerler kullanılarak gama-ışınlamasıyla iyileştirilmesi

Review Article

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ABSTRACT

This paper reviews the synthesis and characterization of allyl alcohol based copolymers and their application into woods and the improvement of dimensional, mechanical and biological stability of woods by using gamma-radiation. Selection of monomer and/or monomer pairs, copolymerization, impregnation, gamma-irradiation, artifical ageing, dimensional and mechanical stability, biodegradation of treated woods are mentioned. Novel treatments and technologies are also presented.

Key Words
Copolymerization, impregnation, wood+polymer(copolymer) composite, gamma-irradiation.

ÖZET

Bu makale allil alkol esaslı kopolimerlerin sentezi ve karakterizasyonunu ve gama-ışınlaması kullanılarak bu kopolimerlerin odunlara uygulanması yoluyla odunların boyutsal, mekanik ve biyolojik kararlılıklarının artırılmasını özetlemektedir. Monomer ve/veya monomer çiftlerinin seçimi, kopolimerizasyon, emprenye, gama-ışınlama, muamele görmüş odunların yapay yaşlandırılması, boyutsal ve mekanik kararlılığı, biyobozunmasından bahsedilmektedir. Muamele ve teknolojilerde verilmiştir.

Anahtar Kelimeler
Kopolimerizasyon, emprenye, odun+(ko)polimer kompozit, gama-ışınlama.

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INTRODUCTION

Wood is an important raw material which has been used by human beings since early years. In today's world, parallel to the technological developments the number of fields where the raw material of wood is usage increased and it has not lost its importance as a raw material.The reason for the diversity of why the fields where wood is used too much is related to its anatomical structure, physical and mechanical properties and its chemical composition. The properties which make wood important among other raw material sources are its widespread occurrence, stability, hardness, lightness, elasticity and being a renewable source[1].

The conservation of wooden objects is almost as old as its usage. The methods of conservation include every kind of technical, physical and chemical process that prolongs the period of use by increasing the resistance to the changes in the dimensions with moisture uptake, to fire and to biological degradation. Materials like etheric oils, varnish, oil paint, linseed oil, some paints and tar were used; they carbonised the parts of wooden poles and post that are in touch with the soil, and smoothen the surface. In the Middle Ages the wood was soaked into some protective and antiseptic material such as mercury chloride and arsenic compounds, but in modern times better impregnation materials have been found [2].

Wood is an important raw material that is cheap and easily worked. However, wooden objects are subject to environmental attack and mechanical shocks. The properties of wood can be modified by polymerizing various impregnated monomers with gamma radiation [3]. Wood -plastic composites were prepared for the first time as a result of experimental work done at the University of West Virginia in 1962 [4]. The kind of wood, its anatomic structure, composition, and density, and the viscosity, chemical structure, and polarity of the monomer are important factors in the impregnation of monomers into wood [5]. The wood-plastic composites have greater dimensional stability, compressive strength and hardness than the original wood [6,7].

The studies on the conservation of wooden objects till today can be grouped as follows [1]:

- conservation against biological degradation [5,8],
- conservation against dimensional instabilisation [9–15],
- conservation against mechanical effects [16–21],
- conservation against burning [22,23],
- effects of radiation on wood and wood/(co)polymer composites [24,25].

Despite its various useful properties, wood also possesses some disadvantages. Advantages and disadvantages can be listed as follows [7,26]:

Advantages
- light and strong for its weight,
- easy to work with,
- good insulator of heat and sound,
- elasticity,
- adjusts humidity,
- good appearance,
- easily available.

Disadvantages
- Properties vary,
- material is not homogeneous,
- combustible,
- liable to distortion from moisture,
- liable to damage by fungi and insects

There are four main factors which affect the strength of wooden objects [6,27]:

1. Biological factors (damages due to fungi and insects).
2. Physical factors (fire, humidity).
3. Mechanical factors (breakage, deformation).
4. Chemical factors (effects of acids, bases and salts).

The most important factor is temperature; at high temperatures, woods catch fire. The other important physicalfactor is moisture, because wood is a hygroscopic substance. When the temperature is decreased, the water uptake of wood increases. The changes in the dimensions with the moisture effect is called "working of wood".

The advantage of wood is its presence everywhere. It is stable, hard, light, and elastic and is a renewable resource. Wooden objects also have disadvantages. For instance, dimensional changes may occur in humid atmospheres. Wood is not always durable against fungus or insects: thus its hardness and mechanical strength may not be sufficient. However, researchers have developed methods to remove most of these disadvantages to preserve the value of wooden objects [27,28].

Selection of monomer/monomer pairs

Despite its various useful properties, wood also possesses some disadvantages. The wooden materials are weak against environmental attacks and mechanical shocks and don't possess dimensional as well as biological stabilities. The conservation of wooden objects against various deteriorating agents can best be achieved by proper selection of consolidant material. The used first impregnant is methyl methacrylate (MMA) in USA and styrenes, styrene acrylonitriles and polyester combinations are used [16]. MMA has some disadvantagesand in addition to MMA hexene-1/maleic anhydride, glycidyl methacrylate and the other monomers are used [29,30]. MMA polymerized in the wood by gamma-radiation is found to be improve the dimensional stability of wood but increased the brittleness. This was found to be due to the high radiation damaging the wood. After these monomers the wood properties are tried to improve by impregnation with multifunctional monomers [58]. The impregnation of wood with vinyl monomers is performed by Loos and etc. [20,31-34]. The crucial point is therefore the selection of a monomer or monomer mixture which can protect and consolidate the wood when polymerized in or whose polymer applied to it.

The consolidant action can be improved if the polymer is fully compatible with the chemical constituents of the wood which are cellulose, lignin and hemicelluloses. Since the structures of cellulose and lignin are compatible with allyl alcohol (AA) and allyl 2,3 epoxypropyl ether (AE) monomers, AA and AE have been used in the conservation and consolidation studies [29,35]. Due to the resonance stability of allylic radicals, chain polymerization of allyl monomers is not efficient, and the products obtained have very low molecular weights. To increase its rate of polymerization and improve the properties of its polymer, AA, AE were copolymerized with acrylonitrile (AN) and methyl methacrylate (MMA) monomers. Solpan and etc. focused on the preparation of copolymers of AA, AE with AN or MMA and investigation of the application and effects of these polymers and their copolymers on the wood samples. Consolidant and protective effects of these polymers and copolymers on the wood samples were measured by water uptake, acid rain test, compressive strength testson freshly prepared and artificially aged samples [3].

Copolymerization and characterization

Polymeric materials find an extremely wide range of applications in almost every branch of technology. This is mostly due to the combination of diverse properties in a single material. If any specific property of a polymeric material is lacking, then copolymerizing a given monomer with another having the desired property of the starting material can be considered to remedy this defect [36]. Copolymerization is also an effective way of incorporating some poorly polymerizing monomers into a polymeric chain. Allyl monomers are typical examples of monomers which show very low tendencies to homopolymerize [36-38]. In the presence of some active monomers, however, they can be turned efficiently into copolymers. The copolymerization of vinyl monomers with the monomers including epoxy group has brought a new dimension to the polymer chemistry. The usage of allyl compounds that possesses also functional groups as hydroxyl, epoxy and ethylenic unsaturated groups is gradually arousing interest. Despite of the fact that the homopolymerization of allyl ether compounds is very difficult to perform, their copolymers were obtained easily. Two of the important members of allyl monomers, namely allyl alcohol, allyl 2,3 epoxy propyl ether can be copolymerized with some vinyl monomers. As the homopolymerization of allyl monomers is rather difficult, their copolymerization has received more attention. Allylic monomers copolymerize with reactive monomers, forming mixtures of copolymer and homopolymer of the reactive monomer if the polymerization is forced to high conversions. The allylic monomer lowers the molecular weight of the product and, can not be incorporated into the copolymer in greater than 50 mol% quantities due to the poor homopolimerizability of the allyl monomer [39-42], acquired the copolymerization of allyl acrylate with styrene and they determined that about 3% of the allyl groups take part in copolymerization and the copolymer could be converted to crosslinked structures through the residual allyl groups.

Homopolymerization of AA and AE initiated by gamma rays and the copolymerization of AA, AE with acrylonitrile (AN) and methyl methacrylate (MMA) were investigated [37]. Copolymerization of AA and AE with acrylonitrile (AN) initiated by γ-rays has been investigated to determine the respective reactivity ratios. One of the major aims in copolymerization studies is to determine the reactivity ratios of corresponding monomers. In order to determine the reactivity ratios (r_1 and r_2) of monomers used in the copolymerization, monomer mixtures in the different feed compositions were copolymerized to low conversions (5%) [39]. The copolymer samples were analyzed indirectly by using spectroscopic techniques like ultraviolet and infrared and directly by elemental analysis. For the determination of reactivity ratios, different calculation methods were applied to the data collected on the monomer compositions of the feed and copolymers. These methods comprise the Fineman-Ross [43], Kelen-Tüdös [44], Non-Linear Least Square analysis [45,46] and Q-e method of Alfrey and Price [47]. It has been concluded that data obtained from elemental analysis as applied to the Non-Linear Least Square approach gave the most reliable reactivity ratios as 2.09 and 0.40 for acrylonitrile and allyl alcohol, fort he other copolymer obtained AN and AE, reactivity ratios as 2.33 and 0.34 for AN and AE, respectively.

In polymer and plastic science and technology, thermal methods of analysis find very wide use. Plastics encounter elevated temperatures at almost every step in the manufacturing, compounding and processing stages, and even in service, therefore a great deal of information is needed about their thermal behavior. Among different thermal analysis systems, dynamic thermogravimetry is a technique frequently used due to its simplicity and the advantage that only one thermogram is needed for the determination of all of the kinetic constants [37,48]. In dynamic thermogravimetry, since the sample is heated at a controlled heating rate, it is subjected to continuously changing (increasing) temperatures. The thermal stabilities of the homopolymers and copolymers were determined and their degradation activation energies calculated. The copolymers, P(AA/AN), P(AE/AN), obtained from AA+AN, AE+AN monomers were more stable thermally than those copolymers, P(AA/MMA), P(AE/MMA) formed from AA+MMA, AE+MMA monomer mixtures. Two of the important allyl monomers, namely allyl alcohol, allyl glycidyl ether [36,49], have been copolymerized with acrylonitrile and methyl methacrylate monomers, and the thermal stability of the homopolymers of these two monomers have been compared with that of the copolymers.In addition to the epoxy group, the copolymer obtained had residual double bonds which could be used in the crosslinking process [50]. It was seen that the swelling in organic solvents and water and hydrolytic resistance of copolymers were high and their thermal stability and mechanic properties were improved. The thermal characterization of resulting homopolymers and copolymers were realized by Thermal Analysis Techniques and their degradation activation energies were calculated.

Selection of woods and impregnation

Step by step, polymeric materials replace wood in many applications, but still there is no material that can takereplace wooden objects as a whole [26]. Wooden objects have also some disadvantages. For instance, wood changes its dimensions in humid environment, it is not always resistant to fungi or insects and sometimes its hardness and mechanical strength are not sufficient. Methods were developed to overcome the disadvantages of wooden objects.Wood is a very porous material, 70% of its volume is made up of air-filled lumen, the remaining 30% is woodsubstance, or cell walls (wood constituents). Distinct anatomical differences exist between the gymnosperms (softwoods) and the angiosperms (hardwoods) [9,51,52]. The softwoods are fairly homogeneous as they consist basically of only two cell types, the longitudinal tracheids and the ray cells. Hardwoods, on the other hand, are composed of mixtures of four or five cell forms and are thus relatively heterogeneous in their structure [7,53].

Four types of woods selected for conservation, namely beech (hardwood, East Beech, Fagus Orientalis Lipsky), spruce (softwood, East Spruce, Picea Orientalis Lipsky), oak (hardwood, Quercus Cerris Lipsky) and cedar (softwood, Cedrus Libanotica Link) [29] were cut into 3x3x3 cm^3 dimensions.Specimens containing knots or other defects [3] were discarded and then all pieces were brought to constant weights in a vacuum oven kept at 30°C before impregnation. Samples and untreated samples were then chosen at random. Samples were placed in the impregnation chamber, which was evacuated to a pressure below 25 mmHg and left for 15 min. The selected monomers or monomer mixtures (AA, AE, AN, MMA, AA/AN, AE/AN, AA/MMA, AE/MMA) were then introduced until atmospheric pressure was attained. The monomer uptake of the samples was followed. The minimum time required for maximum impregnation of monomer and monomer mixtures into the wood samples was determined. The chamber was then left at room temperature at ambient pressure for the predetermined time to obtain complete impregnation. The minimum time required for maximum impregnation of AN, AA/AN and AE+AN into wood samples was determined to be 24 hours and 5 hours, respectively. For MMA, AA/MMA and AE+MMA, 30 hours and 8 hours, respectively. The monomer impregnated wood samples were carefully weighed, wrapped in aluminum foils and irradiated with gamma rays at a dose rate of 0.87 $kGyh^{-1}$. Typical monomer loading curves were determined gravimetrically. % Conversion of these monomers into homo or copolymers within the wood matrix was investigated in the different irradiation doses.

The effect of Gamma-irradiation

New materials like plastics often replace wood, which has disadvantages such as lack of hardness, mechanical strength, and inferior biological stability [54]. Many of the problems of wood can be eliminated, thus increasing the value of the material. Conservation of wooden materials is important economically, and depends on the structure of the wood, where it is to be used, the impregnation method and the enforcing materials used. The first detailed study of this subject was conducted in 1909. To increase the dimensional stability of wood, the pores are filled with resin impregnants [4,6,7,55].

In order to increase the dimensional stability of wooden objects, filling the pores of the wood is a practical and useful method [1]. Since wood is anisotropic, during uptake and release of moisture it changes its dimensions in three different directions so it does not own dimensional stability.Wood is a very porous material, about 70% of the volume is made up of air-filled cells. The remaining 30% is wood substance, or cell walls (wood constituents). Although wood is considered a highly porous material, it is not always highly permeable and shows great variability in permeability both within and between species. Important existing processes that are strongly influenced by wood permeability are seasoning, wood preservative and fire retardant treatments, and pulping. The efficiency of these treatments, which in turn is related to cost, is largely controlled by the anatomical structure of the wood. Distinct anatomical differences exist between the gymnosperms (soft woods) and angiosperms (hardwoods) [51,52]. The softwoods are fairly homogeneous as they consist basically of only two cell types, the longitudinal tracheids and ray cells. Hardwoods, on the other hand, are composed of mixtures of four or five cell forms and are thus relatively heterogeneous in structure [7,53].

Wood is a heterogeneous material that is formed up of two major components, carbohydrate and lignin, and two subcomponents that are organic extractives and inorganic minerals. Despite its various useful properties, wood also possesses some disadvantages as showing dimensional instability and anisotropic mechanical properties [35]. A new development in the conservation of wood is the irradiation of wood impregnated with various monomers by a 60Co γ-source. Wood behaves as a matrix for polymers and copolymers and many of its original properties are developed in the wood/(co) polymer composites. The materials prepared as a result of the polymerization of impregnated liquid monomers withhigh-energy radiation are called "wood/plastic composites" [4,8,24,34,56-58]. The advantages of the radiation polymerizationin the wooden materials can be summarized as follows:

- Application is simple and cheap.
- The reaction rate can be controlled easily.
- Since the monomers have low viscosity, they can diffuse easily into wood along the fiber direction.Sterilization can be achieved simultaneously by γ-irradiation.
- High-penetrative γ-irradiation technique can be applied to any size of the material.

The success of the conservation and consolidation processing ofwood depends on the impregnation of sufficient monomer into the wood and the degree of polymerization[28]. In order to start polymerization, radiation and thermal initiators are needed. Wood is a matrix for polymer and copolymers. When compared with the original wood, many desirable properties are developed in the structure of woodpolymer (copolymer) composites. These developments consist of chemical resistance, resistance against burning, resistance against fungus and bacteria, durability and decrease in the water uptake, and dimensional stability. When the monomer mixtures are impregnated into the wood, the pores of the wood decrease and the resistance of the wood against moisture absorption increases [4,16,58,59-61].

The irradiation of monomers impregnated into the wood changes the properties of the wood. Wood resists γ-radiation because it consists of ligninand cellulose. The effect of high radiation on wood has been previously investigated [25, 60,62]. Lignin is the most radiation-resistant component, because of its aromatic groups, protecting carbohydrates from radiation. For doses over 100.0 kGy, the mechanical properties of wood may weaken. These effects do not depend on the dose rate [10,60].

Because wood is a natural material, the data reported are averages of eight samples for each test. To prepare the wood samples to artificial aging test, original and consolidated wood pieces were kept in the environmental chamber for 28 days in repeated hourly cycles between -40°C and +40°C [3].

Wood substances behave as a three-dimensional network of polymeric materials. Certain properties of wood can be changed by impregnation with these materials. The properties then depend on the amounts of polymer within the cell lumens. This amount is influenced by the relative sizes of penetrant molecules and of effective lumens in the cell walls [2,63,64]. In order

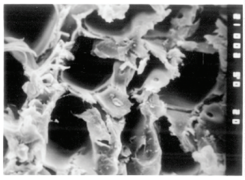

Figure 1 SEM photograph (x500) of untreated cedar.

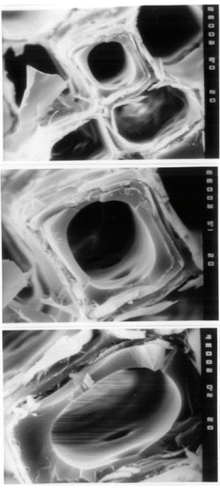

Figure 2 SEM photograph (x800),(x1500), (x2000) of P(AA/MMA)loaded cedar.

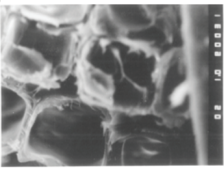

Figure 3 SEM photograph (x1000) of P(AE/AN) loaded cedar.

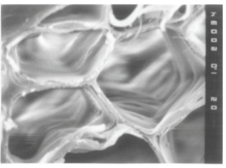

Figure 4 SEM photograph (x1000) of P(AE/MMA) loaded cedar.

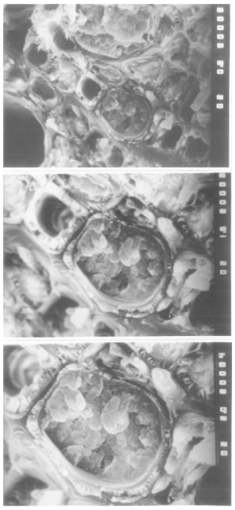

Figure 5 SEM photograph (x800),(x1500), (x2000) of PAN loaded oak.

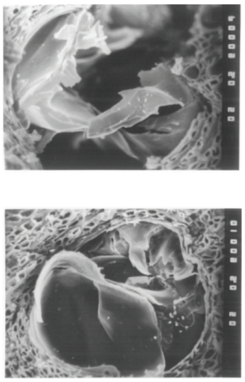

Figure6 SEM photograph (x200),(x200) of P(AA/AN) loaded oak.

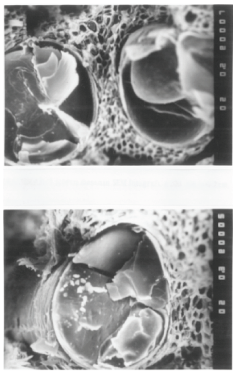

Figure 7 SEM photograph (x200),(x300) of PMMA loaded oak.

to investigate the interaction and compatibility between copolymers, detailed Scanning Electron Microscopic (SEM) studies were also carried out on these samples.

SEM photographs of wood-polymer (copo1ymer) composites show that the porous structure of the wood is filled with homopolymers and copolymers (Figures 1-7). The strong bonding between the cell wall of the wood and homo and copolymers is especially apparent in micrographs of the broken surfaces of the oak-MMA composite. AN monomer and AE/AN monomer mixtures were homopolymerized and copolymerized heterogeneously (a popcorn structure is visible) [54], whereas for MMA and AE/MMA, homopolymerization and copolymerization were carried out homogeneously. It has been observed that copolymer obtained from AE and MMA mixture showed the optimum compatibility.

Water uptake capacity of the untreated wood and wood/(co)polymer composites

The water uptake capacity (in wt.-%) was determined as the weight increase of the untreated wood/(co)polymer composites immersed into distilled water (30 days, pH = 6.7) in relation to the dry weight of the wood. The dimensional stability of impregnated wood samples was evaluated with ASE (anti-swell efficiency, anti-shrink efficiency) and the values of percent volume change [20]. In order to investigate the dimensional stability, the volume change (ΔV) and ASE values were acquired. For the determination of ASE, the dimensions of the wood/(co)polymer composites and untreated wood samples before and after the beginning of their water uptake capacity were measured.For spruce/PMMA and spruce/P(AE/MMA) composites have the lowest water uptake capacity. Spruce is a very porous, its density is low. Since the quantity of polymer and copolymer in the spruce samples is very high, the water uptake capacity of untreated spruce is also huge. Initial water uptake capacity of untreated spruce decreased from 94% to 40, 50 and 30% in the presence of PMMA, P(AE/AN) and P(AE/MMA), respectively.

Change of the compressive strength and Brinell hardnessnumber (BHN) with conversion

In order to understand the mechanical behavior of untreated wood and wood(co)polymer composites, the compressive strengths of the wood/(co)polymer composites and untreated woods were measured parallel and perpendicular to the fiber direction, since wood is a fibrous material and, therefore, different results are obtained depending on the direction of the applied force. The compressive strength depends on the chemical composition and the anatomic structure of the wood, the irradiation dose, the artificial aging process, and the types of polymer and copolymer used in the wood [35].The Brinell hardness numbers of wood/(co)polymer composites were determined. The change in the Brinell hardness numbers (BHN) of wood samples irradiated with various doses (various conversions) are determined for wood/(co) polymer composites. The BHN results indicate the surface hardness and show differences for various surfaces [19,65].

The biodegradation of the untreated wood and wood+copolymer composites

The wooden objects degrade biologically and physically. Woods are damaged on a large scale because of the destructive effects of insects, mould, microorganisms and fungus [2]. We can prevent this destruction by impregnating the wood with appropriate preservative materials. The presence of the fungus and microorganisms can be ascertained only by providing proper conditions [17]. The presence of polymer and copolymer in the wood samples causes an increase in the stability of wood against fungi and bacteria. The reason for this is not the deposition of toxic material in the wood but that the wooden objects cannot take up enough water for the development of fungus in the presence of polymer or copolymer[1]. The use of gamma rays for the polymerization in wood also causes sterilization and prevents the reproduction of similar structures.

Conclusion

As a consequence, PAN, P(AGE/ AN), PMMA, P(AGE/MMA) homopolymers and copolymers increased the mechanical strength of the wood, thus protecting the samples against aging with respect to the untreated woods. The percent modification in compressive strength of these systems depends on the type of monomer used. The addition of AE to either AN or MMA provides better mechanical resistance for the wood samples. It is also found that the AE/MMA copolymer is most effective in protecting the wood against various environmental attacks.

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