Modification of Some Mechanical Properties of Cedar Wood by Radiation Induced In-situ Copolymerization of Allyl Glycidyl Ether with Acrylonitrile and Methyl Methacrylate

Dilek Şolpan* and Olgun Güven
Hacettepe University, Department of Chemistry, 06532, Beytepe, Ankara, Turkey

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ABSTRACT

Acrylonitrile (AN), methyl methacrylate (MMA), allyl glycidyl ether (AGE), AGE+AN, AGE+MMA monomer and monomer mixtures were used to conserve and consolidate the wood. The fine structure of wood-polymer (copolymer) composites were investigated by scanning electron microscopy (SEM). The copolymer obtained from AGE+MMA monomer mixture showed the optimum compatibility. Compressive strength and Brinell hardness number (BHN) measurements of the wood-polymer(copolymer) composites indicated that their mechanical stability is increased. The increase in the compressive strength that is in perpendicular to the fibres in the highest conversion, is 197% in cedar wood in the presence of P(AGE/MMA). It is found that the mechanical stability of the woods that imply AGE+AN and AGE+MMA copolymers is higher than the others. There was almost no change in the mechanical stability and BHN after 28 days of the ageing process.

Key Words: wood-plastic composites, gamma-ray, mechanical tests of woods, allyl glycidyl ether

INTRODUCTION

A practical and usable method to increase the mechanical stability of the wooden objects is to fill the pores of the wood. This is possible only when the impregnation materials and the application of the appropriate impregnation method are known [1].

With the development of polymers and plastic age, researchers found a new chemical conserving technique for wood. The composites that are formed up of natural and artificial polymers have been regarded as new and potential materials [2]. Monomer solutions are impregnated to the wood which serves as a matrix and polymerize the monomers. Consequently, the mechanical and physical properties of the wood are improved [3–6].

The success of the conserving and consolidating process of the wood depends on the impregnation method of the wood, the types of monomers and the degree of polymerization [4]. Polymerization of the

(*) To whom correspondence should be addressed.

liquid monomers with high energy radiation and gamma radiation is very suitable for this purpose.

Selection of the monomer which can protect and consolidate the wood when polymerized in or applied to it is very important. The consolidant action can best be obtained if the polymer is fully compatible with the chemical constituents of the wood such as cellulose, lignin and hemicelluloses. Since the structures of cellulose and lignin are compatible with AGE, the latter was selected as the monomer in this work. The polymerization of AGE does not take place efficiently. The aim of this study is to prepare copolymers of AGE with AN and MMA and to investigate the application and the effects of these monomer and monomer mixtures to the cedar samples. By impregnation of the monomer and monomer mixtures to the cedar in different dimensions, a protective system is tried to be developed and the properties that are gained to the cedar wood by polymers and copolymers are determined by using hydrolic press and artificial aging methods.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), acrylonitrile (AN), and allyl glycidyl ether(AGE) were supplied from BDH and Merck Companies, respectively.

1-propanol, obtained from Fisher, as a non-solvent and for removing the monomers, which are not polymerized in the wood-polymer(copolymer) samples, was used. All the chemicals were used without further purification.

Preparation of the Wood Samples

The cedar (softwood) (Toros cedar; Cedrus Libanotica Link) samples used in the study were taken from Antalya where it is their natural spreading zone.

The cedar samples were cut into 3×3×3 cm^3 dimensions and the surfaces were soothed carefully in order to avoid as far as possible blocking of the pores. The wood samples were dried for 48 h at 30 °C in a vacuum oven and then weighed (data reported are the averages of eight samples for each test).

The minimum time required for maximum impregnation of monomer and monomer mixtures (MMA, AN, AGE/AN, AGE/MMA) into wood(cedar) samples was determined. The impregnated cedar samples were then irradiated by a ^{60}Co-γ source at a dose rate of 0.85 kGy per hour. After irradiation, the wood-polymer(copolymer) composites were recovered through extensive drying to remove the excess monomers. The amount of polymer and copolymer in the wood-polymer(copolymer) composite was determined by the percent polymer loading in terms of weight.

Characterization of Wood-Polymer Composites

Mechanical Test

Mechanical tests were carried out in a 100 ton hydrolic press (SBL Model CT-250A) and the wood samples of 3×3×3 cm^3 dimensions were used. The compressive strengths perpendicular and parallel to the fibres of wood-polymer(copolymer) composites and untreated cedar samples were determined. The quantity of load at the time of the beginning of deformation was based on definite height. The compressive strength was carried out according to the German Industry Norm (DIN) 52185(1954) procedures.

The compressive strength perpendicular to the fibres of wood-polymer(copolymer) composites and untreated wood samples were also determined before and after artificial aging treatment and thus a comparison was made between the aged and unaged samples.

Hardness Test

The hardness tests were performed with a HP025 model hardness testing machine on untreated cedar and wood(cedar)-polymer(copolymer) composites.

The hardness is determined by forcing a hard indenter into the surface of the material to be measured. The Brinell indenter is a steel ball 5 mm in diameter, usually pressed under a Vickers load of 5 kg. (A 5 kg load is used for soft materials like woods). The diameter of the indentation is related to the hardness.

Artificial Aging Test

The resistance of wood samples consolidated with

homo- and copolymers against artificial aging was checked by mechanical test. Original and consolidated wood pieces were kept in the environmental chambers in 28 days in repeated hourly cycles between –20 °C to +40 °C.

RESULTS AND DISCUSSION

In this study, the allyl glycidyl ether(AGE) monomer that is compatible with the major components of the wood was used for consolidating and conserving the wooden material.

The minimum time for the impregnation of AN and AGE+AN, MMA and AGE+MMA monomer and monomer mixtures was determined. For AN and AGE+AN, 24 and 5 h, and for MMA and AGE+MMA, 30 and 8 h were required, respectively. For these predetermined times the cedar wood samples that were immersed in the monomer and monomer mixtures were irradiated by the ^{60}Co-γ source at different doses.

The polymer and copolymer conversion in the wood were determined gravimetrically. The monomer loading curves are given in Figures 1 and 2. The conversion of AN, AGE+AN monomer and monomer mixtures to homopolymer and copolymer was determined for 4.0–25.0 kGy irradiation doses (Figure 1).

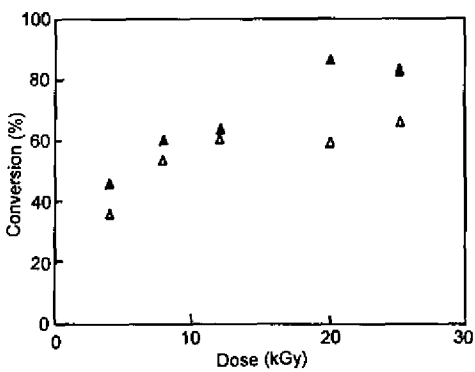


Figure 1. Conversion of monomer and monomer mixtures into homopolymer and copolymer with radiation in cedar. Monomer feed ratio of AGE/AN is 1:1. (Δ) AN, (▲) AGE/AN.

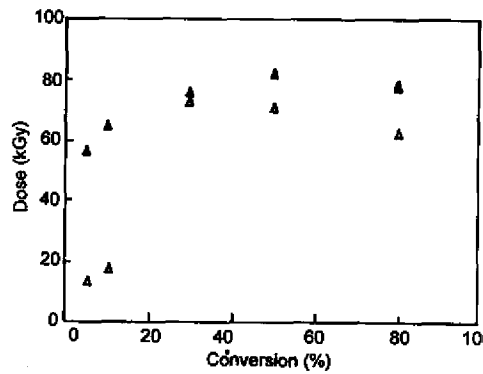


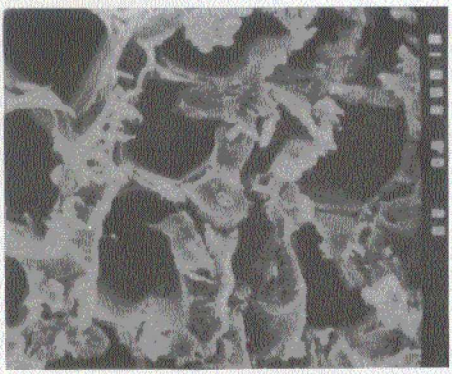
Figure 2. Conversion of monomer and monomer mixtures into homopolymer and copolymer with radiation in cedar. Monomer feed ratio of AGE/MMA is 1:1. (Δ) MMA, (▲) AGE/MMA.

The conversion of monomer and monomer mixtures into homo- and copolymers in the cedar samples impregnated with MMA, AGE+MMA, were investigated between 5.0–80.0 kGy irradiation doses (Figure 2).

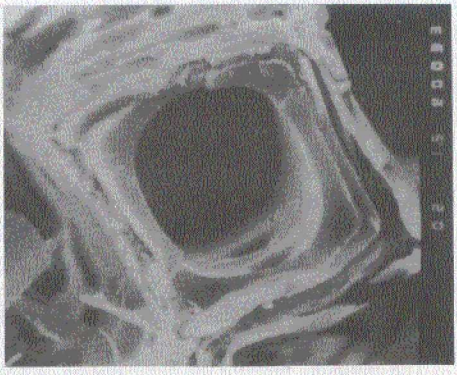
Certain properties of wood can be changed by impregnation with polymeric materials [5, 7]. The properties then depend on the relative amounts of polymer within the cell lumens. The fine structure of wood-polymer(copolymer) composites were investigated by SEM. In order to investigate the interaction and compatibility between homo- and copolymers, detailed SEM studies were carried out on these samples. The effectiveness of wood conservation depends to a large extent, on their penetration and distribution within the wood substrate. With SEM, the distribution of many commonly used conservants can be followed at the cellular level [8].

In Figure 3(a) the SEM photograph of untreated cedar at ×500 magnification is given and SEM photograph of PAN-treated cedar at ×800 magnification is seen in Figure 3(b). In Figures 3(c) and 3(d), SEM photographs of P(AGE/MMA)-treated cedar at ×1500 and ×2000 magnifications are given.

The cedar wood has a porous structure as it is evident in Figure 3 (a) and its microstructure is simple. SEM photographs explain the high conversion



(a)



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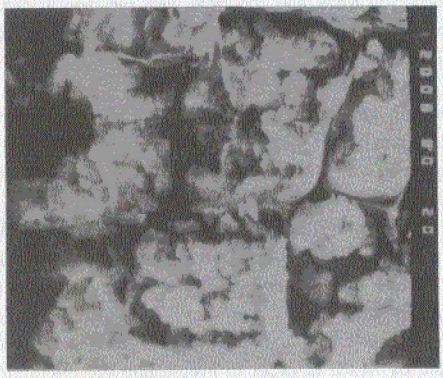
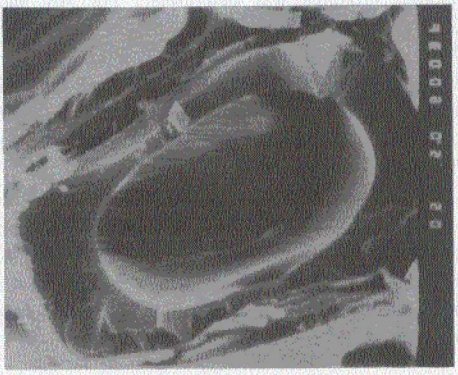


(b)



(d)

Figure 3. SEM photographs of: (a) untreated cedar×500, (b) PAN- loaded cedar×800, (c) P(AGE/MMA)-loaded cedar×1500, (d) P(AGE/MMA)-loaded cedar×2000.

of impregnated monomers and monomer mixtures to polymers and copolymers for cedar wood in parallel to the impregnation degree.

Figure 3(b) shows that only the inner surface of the cell lumens is filled with impregnated AN homopolymer since AN is polymerized heterogeneously. Figures 3(c) and 3(d) show the filling behaviour of copolymer P(AGE/MMA) being in interaction with the outside surface of the cell lumens as well, because AGE/MMA and MMA are copolymerized and polymerized homogeneously. The same situation is valid for the copolymers AGE/AN prepared heterogeneously and AGE/MMA copolymers prepared homogeneously.

Mechanical Test

Variation of Compressive Strength and Brinell Hardness Number with the Conversion

The compressive strengths in the parallel and perpendicular directions to the fibres in the wood samples that are polymerized by impregnated monomer were measured. Since wood is a fibrous material, different

results were obtained depending on the direction of applied force. The compressive strength depends on the chemical composition of the wood, the anatomic structure, the kind and amount of polymer and copolymer used, the irradiation dose and the effect of radiation on wood and the aging process.

In Figures 4 and 5, the change in the compressive strength of wood samples in the presence of PAN, P(AGE/AN) and in the presence of PMMA, P(AGE/MMA), irradiated to various doses (various conversions) are given, respectively.

Variation of compressive strength with polymer and copolymer loading (irradiation time) is given in Figures 6 and 7. The compressive strengths parallel and perpendicular to fibres of wood samples in the presence of P(AGE/AN) and P(AGE/MMA) are higher than the wood samples in the presence of PAN and PMMA.

The change of the compressive strength parallel and perpendicular to fibres with the irradiation dose in untreated cedar is seen in Table 1. The changes at low irradiation dose are not significant, however, at 140.0 and 200.0 kGys irradiation doses compressive strengths parallel and perpendicular to fibres were decreased. The effect of high radiation on wood has been investigated by various authors.

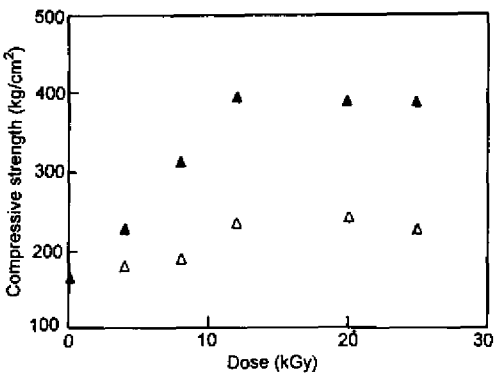


Figure 4. Compressive strength of cedar impregnated with monomer and monomer mixtures depending on the irradiation dose. Monomer feed ratio of AGE/AN is 1:1. Compressive strength taken perpendicular to the fibres. (Δ) AN, (▲) AGE/AN.

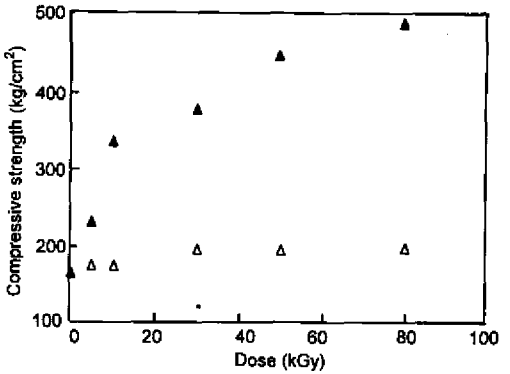


Figure 5. Compressive strength of cedar impregnated with monomer and monomer mixtures depending on the irradiation dose. Monomer feed ratio of AGE/MMA is 1:1. Compressive strength taken perpendicular to the fibres. (Δ) MMA, (▲) AGE/MMA.

As Munnikendam [9] determined in his study, lignin is the most radiation-resistant component due to its aromatic groups, protecting carbohydrates from radiation. At doses over 100.0 kGy, the possible decrease in the mechanical properties of wood can be followed from the results given in Table I [10].

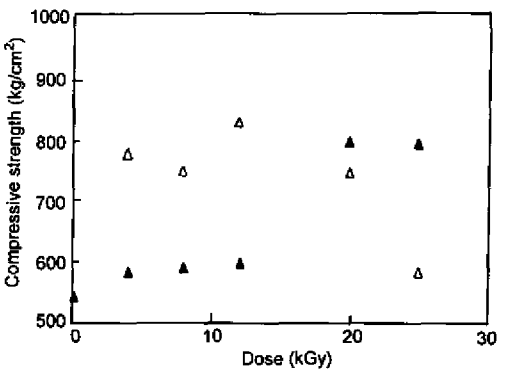


Figure 6. Compressive strength of cedar impregnated with monomer and monomer mixtures depending on the irradiation dose. Monomer feed ratio of AGE/AN is 1:1. Compressive strength taken parallel to the fibres. (Δ) AN, (▲) AGE/AN.

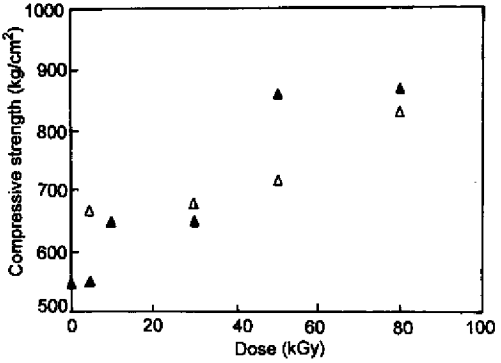


Figure 7. Compressive strength of cedar impregnated with monomer and monomer mixtures depending on the irradiation dose. Monomer feed ratio of AGE/MMA is 1:1. Compressive strength taken parallel to the fibres. (Δ) MMA, (▲) AGE/MMA.

The change in increase of the compressive strength parallel and perpendicular to the fibres with irradiation dose in wood(cedar)-polymer(copolymer) composites is given in Table 2. In all wood-polymer(copolymer) composites, when the irradiation dose increases the quantity of polymer(copolymer) in wood also increases [11, 12]. In the presence of PAN, P(AGE/AN) and in the presence of PMMA, P(AGE/MMA), the change of BHN with the irradiation dose is depicted in Figures 8 and 9, respectively. BHN increases when the irradiation doses (percent polymer) increase. The anatomic structure differences in perpendicular and parallel directions is very

Table 1. The change of the compressive strength parallel and perpendicular to fibres with the irradiation dose in untreated cedar samples.

Dose (kGy)	Compressive strength (k/cm²)	
	Perpendicular to fibres	Parallel to fibres
0.00	167	546
4.00	167	546
5.00	167	546
8.00	167	546
10.00	169	546
12.00	169	540
20.00	168	540
25.00	169	536
30.00	167	536
50.00	167	536
80.00	167	536
140.00	162	540
200.00	162	540

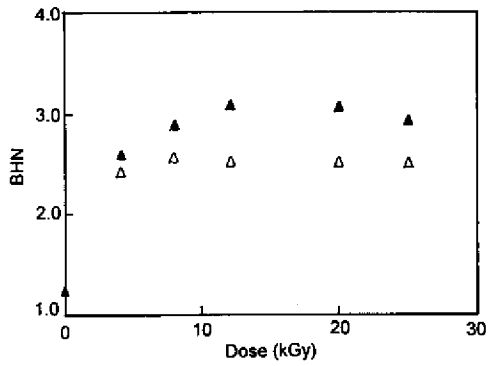


Figure 8. The change of Brinell Hardness Number for cedar samples irradiated in the presence of monomer and monomer mixtures. Monomer feed ratio of AGE/AN is 1:1. (Δ) AN, (▲) AGE/AN.

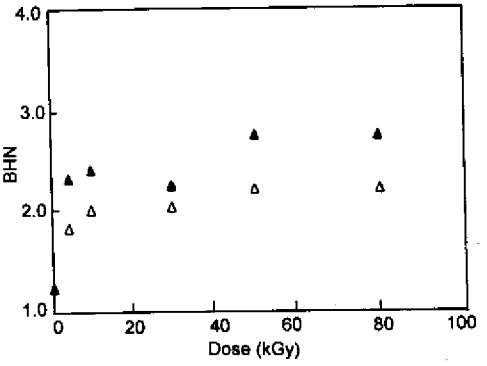


Figure 9. The change of Brinell Hardness Number for cedar samples irradiated in the presence of monomer and monomer mixtures. Monomer feed ratio of AGE/MMA is 1:1. (Δ) MMA, (▲) AGE/MMA.

Table 2. The change of percentage increase in the compressive strength perpendicular and parallel to fibres with irradiation dose and percentage conversion in cedar-polymer (copolymer) composites.

Wood-polymer (copolymer) composites	Dose (kGy)	Conversion (%)	Increase in compressive strength (%)	
			Perpendicular to fibres	Parallel to fibres
CPAN	0.00	0		
	4.00	46	7	44
	8.00	54	13	38
	12.00	61	40	53
	20.00	60	47	38
	25.00	67	38	7
CP(AGE/AN)	0.00	0		
	4.00	35	38	6
	8.00	60	91	8
	12.00	64	138	10
	20.00	88	137	48
	25.00	85	137	47
CPMMA	0.00	0		
	5.00	13	5	22
	10.00	17	4	19
	30.00	74	18	25
	50.00	71	18	32
	80.00	63	50	53
CP(AGE/MMA)	0.00	0		
	5.00	57	38	1
	10.00	65	104	20
	30.00	76	128	19
	50.00	83	169	58
	80.00	78	170	59

outstanding particularly for woods with low specific weights like cedar [13–15]. Although the irradiation dose is constant per surface area, the physical factors that affect during the impregnation process may create hardness differences on the surface which give rise to different BHN numbers.

Changes of Compressive Strength and Brinell Hardness Number with Artificial Aging on Wood-Polymer Composites

The compressive strengths that are in perpendicular direction before and after aging for 28 days in the presence of PAN, P(AGE/AN) and in the presence of PMMA, P(AGE/MMA) are shown in Figures 10 and 11, respectively. It was found that the mechanical strength of the PMMA, P(AGE/MMA) treated cedar samples is lower than the unaged wood(cedar)-polymer(copolymer) composites and also the mechanical strengths of the PAN, P(AGE/AN) treated aged-cedar samples are lower than the PMMA and P(AGE/MMA) treated aged-cedar samples.

The compressive strength in perpendicular

Table 3. The comparison of BHN in unaged and aged for 28 days of cedar-polymer (copolymer) composites.

Wood-polymer (copolymer) composites	Dose (kGy)	Conversion (%)	BHN	
			unaged	aged
CPAN	0.00	0	1.22	1.40
	4.00	44	2.43	2.38
	8.00	54	2.56	2.55
	12.00	61	2.53	2.48
	20.00	58	2.53	2.44
	25.00	67	2.56	2.52
CP(AGE/AN)	0.00	0	2.30	1.11
	4.00	35	2.88	2.90
	8.00	58	3.35	3.00
	12.00	66	3.70	2.98
	20.00	89	3.59	3.09
	25.00	85	3.79	3.09
CPMMA	0.00	0	1.22	1.11
	5.00	13	1.82	1.79
	10.00	18	1.99	1.92
	30.00	76	2.04	1.99
	50.00	74	2.23	2.20
	80.00	66	2.22	2.00
CP(AGE/MMA)	0.00	0	1.22	1.11
	5.00	56	2.88	2.86
	10.00	67	3.35	3.33
	30.00	75	3.70	3.68
	50.00	81	3.59	3.54
	80.00	78	3.79	3.75

direction to the fibres in presence of PAN in the cedar wood is 230 kg/cm^2 which descends to 221 kg/cm^2 after aging. As the amount of polymer percentage in the cedar samples in the presence of PAN is higher, the decrease in the compressive strength is very low after aging for 28 days. The compressive strength in cedar wood in the presence of PMMA that is in perpendicular direction to the fibres decreased from 200 kg/cm^2 to 192 kg/cm^2. In the unaged cedar composites that imply P(AGE/AN) and P(AGE/MMA), the difference between the compressive strengths is very little.

BHN was determined in wood(cedar)-polymer (copolymer) composites after aging for 28 days. The

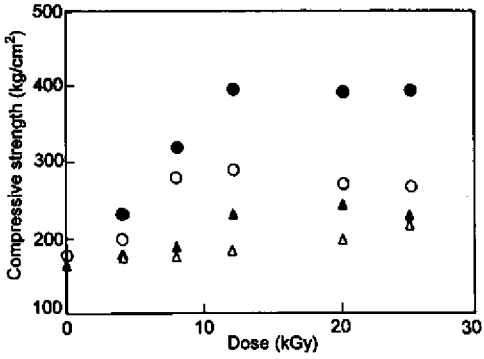


Figure 10. Comparison of compressive strengths of original (solid symbols) and artificially aged (28 days) (open symbols) cedar samples treated with (▲) AN, (●) AGE/AN. Monomer feed ratio of AGE/AN is 1:1. Compressive strength taken perpendicular to the fibres.

results are presented in Table 3.

Since cedar wood has a porous structure, almost all the cells are filled with the polymer. As a result, no important decrease in the hardness value is observed in the aging process applied in very hot and cold media.

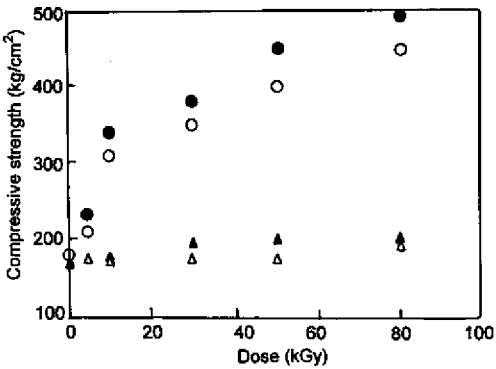


Figure 11. Comparison of compressive strengths of original (solid symbols) and artificially aged (28 days) (open symbols) cedar samples treated with (▲) MMA, (●) AGE/MMA. Monomer feed ratio of AGE/MMA is 1:1. Compressive strength taken perpendicular to the fibres.

CONCLUSION

The mechanical stability of the wood was increased by using P(AGE/AN) and P(AGE/MMA) copolymers.

P(AGE/AN) and P(AGE/MMA) copolymers increased the dimensional stability of the wood.

P(AGE/AN) and P(AGE/MMA) copolymers protected the cedar samples against aging and environmental attacks.

ACKNOWLEDGMENTS

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