Improvement of Mechanical Stability of Beechwood by Radiation-Induced *in situ* Copolymerization of Allyl Glycidyl Ether with Acrylonitrile and Methyl Methacrylate

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ABSTRACT: Acrylonitrile (AN), methyl methacrylate (MMA), allyl glycidyl ether (AGE), AGE + AN monomer, AGE + MMA monomer, and monomer mixtures were used to conserve and consolidate beechwood. After the impregnation of these monomer mixtures in the wood, polymerization was accomplished by gamma irradiation. The fine structures of wood + polymer(copolymer) composites were investigated by scanning electron microscopy (SEM). The copolymer obtained from AGE + MMA monomer mixtures showed the optimum compatibility with the wood. The compressive strength and Brinell hardness numbers determined for untreated and treated wood samples indicated that the mechanical strength was greater in wood + polymer(copolymer) composites than in untreated wood and was greatest in the samples containing AGE + AN and AGE + MMA copolymers. All monomer couples used in this study increased the mechanical strength of the wood and protected the samples against aging. AGE + MMA copolymers were the most effective in protecting the wood against various environmental attacks. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1515–1523, 1999

Key words: wood + polymer composite; gamma irradiation; copolymerization; allyl glycidyl ether; acrylonitrile; methyl methacrylate; mechanical stability

INTRODUCTION

Wood is an important raw material that is cheap and easily worked. However, wooden objects are subject to environmental attack and mechanical shocks. In this study, our aim is to preserve wooden objects against environmental deterioration and mechanical shocks and to consolidate objects already degradated.

The properties of wood can be modified by polymerizing various impregnated monomers with gamma radiation.[1] Wood + plastic composites were prepared for the first time as a result of experimental work done at the University of West Virginia in 1962.[2] 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.[3] The wood + plastic composites have greater dimensional stability, compressive strength and hardness than the original wood.[4,5]

The preservation of wood can best be achieved by proper selection of consolidant materials. The crucial point is, therefore, selecting a monomer that can protect and consolidate the wood. In principle, the consolidant action can be effectively obtained if a polymer is fully compatible with the chemical constituents of the wood. The structures of cellulose and lignin, main constituents of wood, have led us to select allyl glycidyl ether (AGE) as

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a potential monomer for the conservation and consolidation of wood. 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, AGE was copolymerized with acrylonitrile (AN) and methyl methacrylate (MMA) monomers. This study focused on the preparation of copolymers of AGE with AN or MMA and investigation of the application and effects of these polymers and their copolymers on the beechwood samples. Consolidant and protective effects of these polymers and copolymers on the wood samples were measured by compressive strength tests on freshly prepared and artificially aged samples.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and acrylonitrile (AN) were obtained from BDH, and allyl glycidyl ether (AGE) was supplied by Merck. To remove the monomers that are not polymerized in the wood + polymer(copolymer) samples, 1-propanol (Fisher) was used as a nonsolvent. Beech (east beech, *Fagus Orientalis Lipsky*) samples used in the study were obtained from Trabzon (in north east Turkey), their natural spreading zone. Density of the beech kept in vacuum at 30°C for 48 h was 0.74 g/cm^3.

Preparation of the Wood Samples

The wood was first cut into $3 \times 3 \times 3$ cm^3 blocks. Specimens containing knots or other defects 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 (AN, AGE/MMA, MMA, AGE/MMA) were then introduced until atmospheric pressure was attained. 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. Then the impregnated samples were removed from the chamber, individually wrapped in aluminum foil, and sealed to protect the impregnated monomer or monomer mixtures from evaporating. They were then irradiated by a ^{60}Co-γ source at a dose rate of 0.85 kGy/h. After irradiation at various doses, the unreacted monomers were removed by washing the samples with 1-propanol used as a nonsolvent. The samples were later brought to constant weight in a vacuum oven at 30°C. The conversion of monomers to polymers in the wood was determined gravimetrically.

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.

Characterization of Wood + Polymer(Copolymer) Composites

Mechanical Test

Mechanical tests were carried out with a hydraulic press (SBL Model CT-250A) with a maximum load of 100 tonnes. To understand the mechanical resistance of wood pieces, the compressive strength and Brinell hardness numbers were determined. Because wood is a fibrous material, and different results can be obtained depending on the direction of applied force, the compressive strength was determined both parallel and perpendicular to the fibers. Each value reported herein is the average of eight separate measurements. The compressive strengths of wood + polymer(copolymer) composites and untreated samples were determined. In the measurements of compressive strength, the load at the beginning of the deformation of the wood was taken into consideration with respect to a definite height. The compressive strength was measured according to the German Industry Norm (DIN) 52185 (1954). The compressive strength perpendicular to the fibers of wood + polymer(copolymer) composites and untreated wood samples was also determined before and after artificial aging, enabling us to make a comparison between the aged and the unaged samples.

Hardness Test

The hardness tests were performed with a HP025 hardness testing machine on untreated and

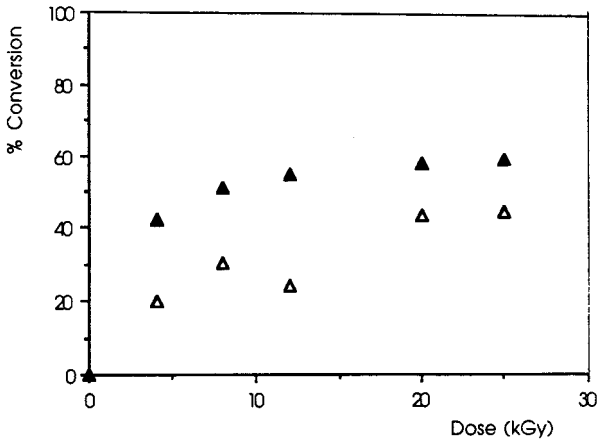


Figure 1 Conversion of monomer and monomer mixtures into homopolymer and copolymer with radiation in beech. Monomer feed ratio of AGE/AN is 1/1. △, AN; ▲, AGE/AN.

treated beech samples. The Brinell hardness numbers (BHNs) were determined in the cross-sectional surfaces of the samples.[6,7] Tests were done by forcing a hard indenter into the surface of the material.[8,9] The Brinell indenter is a 5 mm diameter steel ball pressed under a Vickers load typically of 5 kg for soft materials like wood. The diameter of the indentation is related to the hardness; a hard material naturally exhibits a smaller indentation than a soft one. To measure the diameter of the indented section, a steel ball was allowed to fall on to the wooden sample in 15 sec followed by pressure exerted by the ball for 30 sec, after which the steel ball was released back again in 15 sec. BHN is the load F in kg divided by the surface area of the indentation, where d is the indentation diameter (mm) and D is the ball diameter:

$$\mathrm{BHN} = \frac{F}{(\pi D/2)(D - (D^2 - d^2)^{1/2}} \qquad (1)$$

Compressive strength values and BHN values given in this article are the mean values of eight separate measurements (samples).

Artificial Aging Test

The resistance of wood samples consolidated with homopolymers and copolymers against artificial

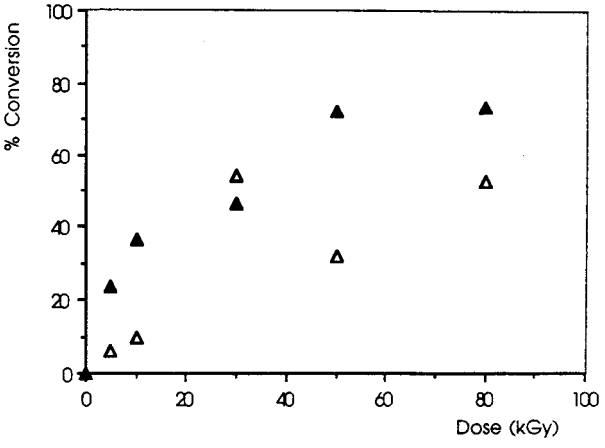
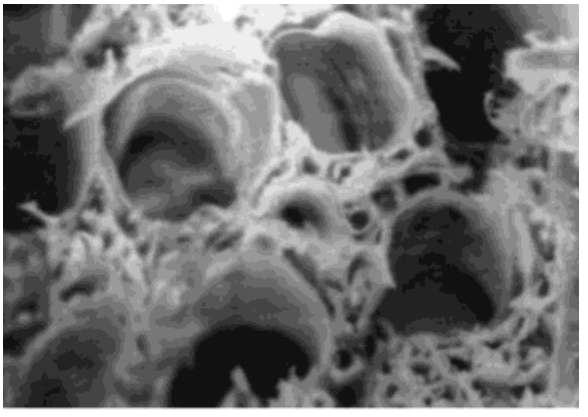
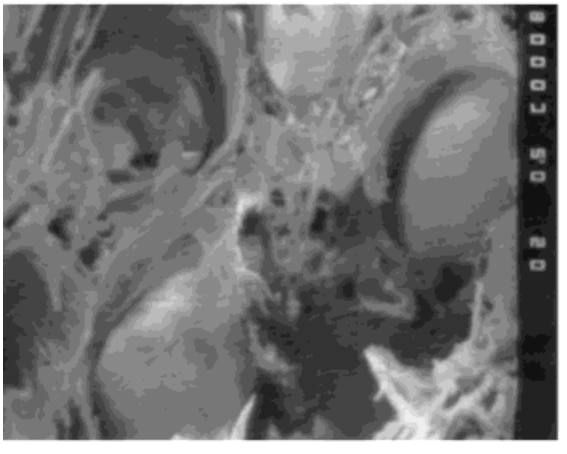


Figure 2 Conversion of monomer and monomer mixtures into homopolymer and copolymer with radiation in beech. Monomer feed ratio of AGE/MMA is 1/1. △, MMA; ▲, AGE/MMA.



(a)



(b)

Figure 3 SEM photograph (×500) of untreated beech (a); SEM photograph (×500) of P(AGE/MMA)-loaded beech (b).

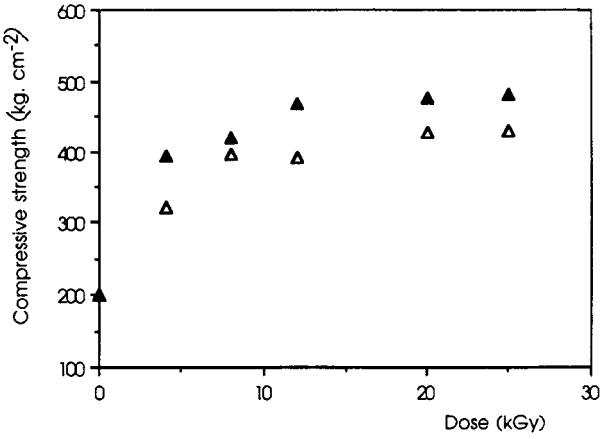


Figure 4 Compressive strength of monomer and monomer mixtures impregnated into beech depending on the irradiation dose. Monomer feed ratio of AGE/AN is 1/1. Compressive strength taken perpendicular to the fibers. △, AN; ▲, AGE/AN.

aging was checked by mechanical testing. In the accelerated artificial aging tests, the wood samples were treated in the following cycles: The samples were placed in special chambers and brought to −40°C in 1 h, kept at that temperature for 2 h, heated up to +40°C in 1 h, kept at that temperature for 2 h, brought to −40°C in 1 h, and so on. The duration of one complete cycle was 8 h. The samples were treated in 3 cycles per day and were removed from the environmental chambers in a 28-day period. The mechanical stability of artificially aged samples was later investigated as mentioned before.

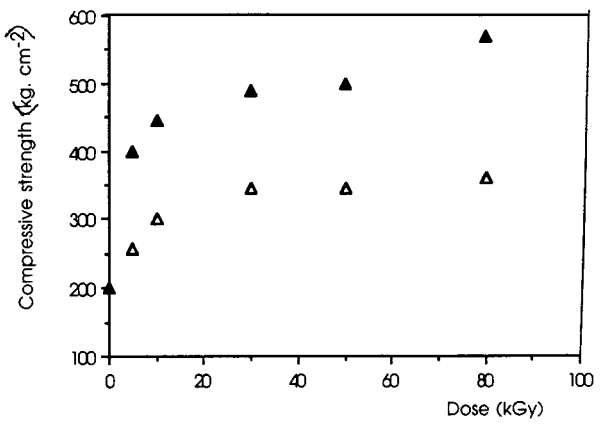


Figure 5 Compressive strength of monomer and monomer mixtures impregnated into beech depending on the irradiation dose. Monomer feed ratio of AGE/MMA is 1/1. Compressive strength taken perpendicular to the fibers. △, MMA; ▲, AGE/MMA.

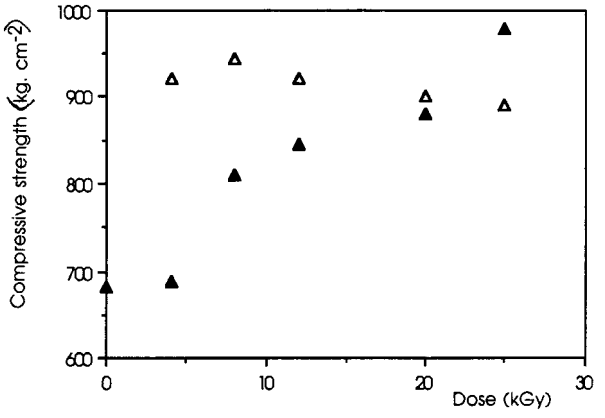


Figure 6 Compressive strength of monomer and monomer mixtures impregnated into beech depending on the irradiation dose. Monomer feed ratio of AGE/AN is 1/1. Compressive strength taken parallel to the fibers. △, AN; ▲, AGE/AN.

RESULTS AND DISCUSSION

To consolidate and conserve wooden objects, AGE and the mixtures of this monomer with AN and MMA were impregnated into the beech samples and polymerized *in situ*.

The feed composition of the monomer couples was initially changed from (3 : 1) to (1 : 3) by volume, and the maximum conversion at a given dose was obtained for a (1 : 1) composition. The other compositions were not used in the study. An equimolar mixture seemed to be the best system to ensure higher yields of copolymer. This is prob-

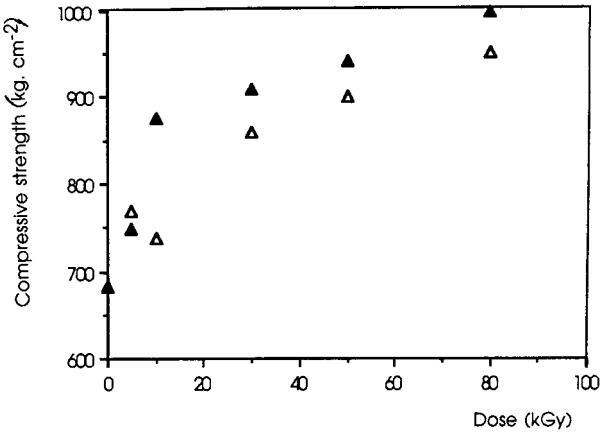


Figure 7 Compressive strength of monomer and monomer mixtures impregnated into beech depending on the irradiation dose. Monomer feed ratio of AGE/MMA is 1/1. Compressive strength taken parallel to the fibers. △, MMA; ▲, AGE/MMA.

Table I Approximate (One Standard Deviation) Statistical Variances in Compressive Strength and Brinell Hardness Number

Wood + Polymer (Copolymer) Composites	Compressive Strength (kg/cm^2)		Brinell Hardness Number (BHN)
	Perpendicular	Parallel	
BPAN	±% 15	±% 20	±% 20
BP(AGE/AN)	±% 5	±% 8	±% 12
BPMMA	±% 6	±% 14	±% 20
BP(AGE/MMA)	±% 3	±% 5	±% 12

ably due to stoichiometric complexation between these two monomers.

The minimum time required for maximum impregnation of into the wood samples was determined to be 24 h for AN and 5 h for AGE + AN, and 30 h for MMA and 8 h for AGE + MMA. The dilution of AN and MMA with AGE seems to have a positive impact on the fluidity of the liquid mixtures. The % conversion of these monomers and monomer mixtures into homopolymers and copolymers within the wood matrix is plotted against irradiation dose in Figures 1 and 2. Higher yields of copolymers were obtained at irradiation doses above 4–5 kGy. The standard deviations for all measurements on beech + (PAN and P(AGE/AN)) are on the order of 1.5–2.0%; those for beech + (PMMA and P(AGE/MMA)) are 1.0–1.2%.

It is known that low-density woods have a high uptake capacity for monomers and other liquids. But the anatomic structure of the wood is more effective than its density. The higher the wood's density, the smaller the cell lumen (pore). Consequently, quantity of the impregnated monomer decreases. The monomers that have high vapor pressures, a small quantity of loss occurs after the impregnation process.[10] In the impregnation of monomer and monomer mixtures into the wood, in addition to above-mentioned factors, the compatibility of the monomers with the chemical constituents of the wood is also a very important factor.

The fine structure of wood + polymer(copolymer) composites were investigated by scanning electron microscopy (SEM). To investigate the interaction and compatibility between homopolymers and copolymers, detailed SEM studies were also carried out on these samples.[11,12] The photographs were taken from the cross-sectional surface of wood samples.

Figure 3(a) gives the SEM photograph of untreated beech at ×500 magnification; Figure 3(b) shows an SEM photograph of P(AGE/MMA)-loaded beech at ×500 magnification. These figures show that almost all of the wood cell lumens were filled by impregnated (AGE/MMA) monomer mixture. The SEM photographs of the wood + polymer(copolymer) composites show that the homopolymer and copolymers PMMA, P(AGE/MMA) fill the lumens of the wood. These microphotographs show that there is a powerful interaction between homopolymer and copolymers and wood samples. It has been observed that copolymer obtained from and AGE + MMA mixture showed the optimum compatibility.

Changes in Compressive Strength and Brinell Hardness Number on Wood + Polymer(Copolymer) Composites

Figures 4 and 5 display the changes in the compressive strength of wood samples in the presence

Table II Change in Compressive Strength Parallel and Perpendicular to Fibers with Irradiation Dose in Untreated Beech Samples

Dose (kGy)	Compressive Strength (kg/cm^2)	
	Perpendicular to Fibers	Parallel to Fibers
0.0	200	682
4.0	200	682
5.0	200	682
8.0	200	687
10.0	196	687
12.0	198	687
20.0	198	680
25.0	198	680
30.0	195	676
50.0	195	676
80.0	194	676
140.0	177	670
200.0	172	670

Table III Change of Percent Increase in the Compressive Strength Perpendicular and Parallel to Fibers With Irradiation Dose and Percent Conversion in Beech + Polymer(Copolymer) Composite

Wood + Polymer (Copolymer) Composites	Dose (kGy)	Percent Conversion	Percent Increase in Compressive Strength	
			Perpendicular to Fibers	Parallel to Fibers
BPAN	0.0	0		
	4.0	20	61	35
	8.0	30	98	38
	12.0	24	96	35
	20.0	43	113	32
	25.0	44	115	30
BP(AGE/AN)	0.0	0		
	4.0	42	97	1
	8.0	51	110	19
	12.0	55	134	24
	20.0	58	138	29
	25.0	59	140	44
BPMMA	0.0	0		
	5.0	6	29	13
	10.0	10	50	8
	30.0	54	73	26
	50.0	32	72	32
	80.0	53	80	40
BP(AGE/MMA)	0.0	0		
	5.0	24	50	10
	10.0	36	122	29
	30.0	45	144	33
	50.0	72	150	38
	80.0	73	184	47

of PAN (polyacrylonitrile), P(AGE/AN) (copolymer of allylglycidyl ether with acrylonitrile) and in the presence of PMMA (polymethyl methacrylate), P(AGE/MMA) (copolymer of allylglycidyl ether with methyl methacrylate), irradiated to various doses (various conversions). The compressive strength of untreated wood sample taken perpendicular to fibers was found to be 200 kg/cm^2. On impregnation and *in situ* polymerization of (AGE/AN) and (AGE/MMA) this value was almost increased to twice that of its original. A comparison of Figures 1 and 2 and 4 and 5 shows that the extent of increase in compressive strength is conversions. When compressive strength tests were made parallel to the fibers, the general trend was the same, except that the numerical values were a little higher. The compressive strength of the original untreated wood samples taken parallel to the fibers was found to be 680 kg/cm^2. The change in this value with polymer and copolymer loading (irradiation time) is given in Figures 6 and 7. The compressive strengths parallel and perpendicular to fibers of the wood samples in the presence of P(AGE/AN) and P(AGE/MMA) is higher than those of the wood samples with PAN and PMMA. The statistical variances of the compressive strength parallel and perpendicular to fibers and BHN are given in Table I.

The changes in the compressive strength parallel and perpendicular to fibers with the irradiation dose in untreated beech are given in Table II. The changes in the low-irradiation dose are not significant, but compressive strengths parallel and perpendicular to fibers were decreased after ~ 25 kGy of irradiation. The effect of high-energy radiation on wood and cellulose has been investigated by various authors. According to Munnikendam and Karpov,[13,14] lignin has been determined to be the most radiation-resistant component, because its aromatic groups protect carbohydrates from radiation.

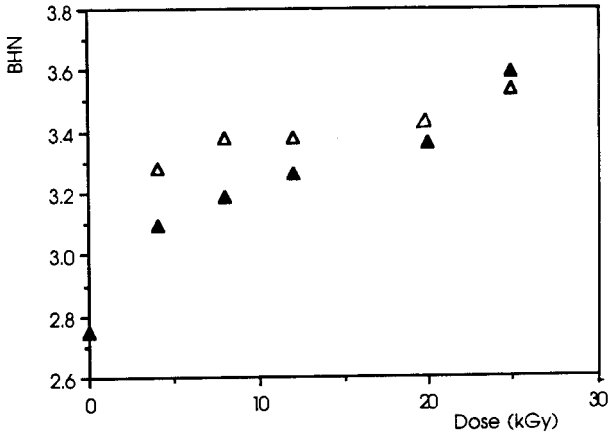


Figure 8 The change in Brinell hardness number for beech samples irradiated in the presence of monomer and monomer mixtures. Monomer feed ratio of AGE/AN is 1/1. △, AN; ▲, AGE/AN.

The change in percent increase in the compressive strength parallel and perpendicular to fibers with irradiation dose in wood + polymer(copolymer) composites is given in Table III. In all of the wood + polymer(copolymer) composites with increased irradiation dose, the quantity of polymer in wood also increases. The percent modification in compressive strength of these systems is dependent on the type of monomer used. The addition of AGE to either AN or MMA provides better mechanical resistance to the wood samples. This is believed to be provided by the epoxy group of AGE. The compressive strength is greatest in the P(AGE/AN) and P(AGE/MMA)-treated samples.[15]

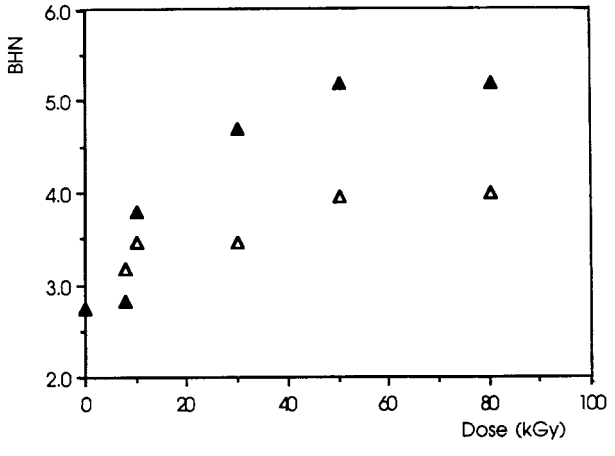


Figure 9 Change in Brinell hardness number for beech samples irradiated in the presence of monomer and monomer mixtures. Monomer feed ratio of AGE/MMA is 1/1. △, MMA; ▲, AGE/MMA.

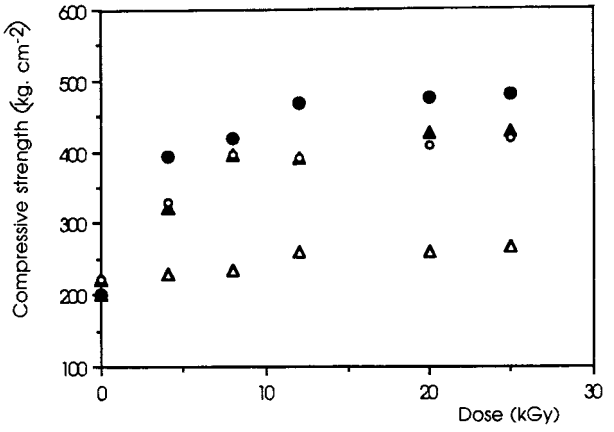


Figure 10 Comparison of compressive strengths of original (solid symbols) and artificially aged (for 28 days) (open symbols) beech samples treated with AN (▲) and AGE/AN (●). Monomer feed ratio of AGE/AN is 1/1. Compressive strength taken perpendicular to the fibers.

The BHNs of wood + polymer(copolymer) composites were determined and compared with those of untreated samples. The changes in BHNs of wood samples irradiated to various doses (various conversions) are given in Figure 8 for beech + PAN and P(AGE/AN) and in Figure 9 for beech + PMMA, P(AGE/MMA). The BHNs determined for untreated and treated wood samples indicated that the mechanical strength of wood + polymer(copolymer) composites increased. The mechanical strength of the wood samples AGE + AN and

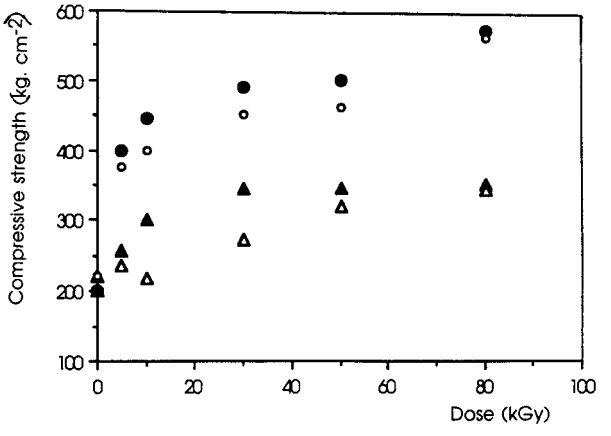


Figure 11 Comparison of compressive strengths of original (solid symbols) and artificially aged (for 28 days) (open symbols) beech samples treated with MMA (▲) and AGE/MMA (●). Monomer feed ratio of AGE/MMA is 1/1. Compressive strength taken perpendicular to the fibers.

Table IV Comparison of BHN in Unaged and Aged (for 28 Days) Beech + Polymer(Copolymer) Composites

Wood + Polymer (Copolymer) Composites	Dose (kGy)	Percent Conversion	BHN	
			Unaged	Aged
BPAN	0.0	0	2.75	2.51
	4.0	19	3.28	3.00
	8.0	32	3.38	3.00
	12.0	24	3.38	3.00
	20.0	43	3.12	2.90
	25.0	44	3.54	3.14
BP(AGE/AN)	0.0	0	2.75	2.51
	4.0	41	3.09	2.96
	8.0	51	3.18	2.98
	12.0	55	3.26	2.98
	20.0	57	3.36	3.14
	25.0	59	3.59	3.42
BPMMA	0.0	0	2.75	2.51
	5.0	6	3.18	3.00
	10.0	10	3.47	3.00
	30.0	52	3.47	3.16
	50.0	36	3.97	3.56
	80.0	56	4.13	4.00
BP(AGE/MMA)	0.0	0	2.75	2.51
	5.0	23	2.82	2.77
	10.0	36	3.79	3.58
	30.0	43	4.71	4.61
	50.0	76	5.20	5.00
	80.0	74	5.19	5.00

AGE + MMA copolymers was higher than that of the samples prepared with pure monomers.

Changes in Compressive Strength and Brinell Hardness Number With Artificial Aging on Wood + Polymer(Copolymer) Composites

The compressive strengths and BHNs of wood samples consolidated with homopolymers and copolymers were compared with those of the samples aged artificially.

The dependence of compressive strength of wood samples on the irradiation dose is shown in Figure 10 for beech + PAN, P(AGE/AN) and in Figure 11 for beech + PMMA, P(AGE/MMA). In these figures the compressive strengths of aged consolidated samples are plotted together with those of unaged consolidated wood samples.

The comparison of BHNs of the aged and unaged wood + polymer(copolymer) composites is also given in Table IV.

After 28 days of aging there were no significant changes in the mechanical stability and BHNs of the composites. Even the lowest compressive strength value for any specific type of treated wood still exceeds that of the original untreated sample.

As a consequence, it was observed that all monomer pairs used in this study increased the mechanical strength of the wood with respect to the untreated beech. It was also found that the AGE + MMA copolymer was the most effective in protecting the wood against various environmental attacks.[16] The use of the AGE + MMA monomer pair for *in situ* polymerization with a total dose as low as 5–10 kGy seems to be quite appropriate to provide mechanical stability to beech.

CONCLUSIONS

The following generalizations can be made:

1. The mechanical strength of the wood was increased by using P(AGE/AN) and P(AGE/MMA) copolymers. The lowest compressive

strength value for beech still exceeds that of original untreated beech.
2. P(AGE/AN) and P(AGE/MMA) copolymers increased the dimensional stability of the wood.
3. P(AGE/AN) and P(AGE/MMA) copolymers protected the beech samples against aging and biodegradation.

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