

The Effect of Moisture Presoaking on Graft Copolymerization of Methyl Methacrylate in Wood Under Mutual Irradiation by Electron Beam Accelerator

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Synopsis

Polymerization of MMA was carried out in wood under mutual electron beam irradiation. The changes in molecular weight (\bar{M}_n , \bar{M}_w) and the number of polymer branches grafted to holocellulose and lignin were compared with the swelling degree (ΔL_{H_2O}) of base veneers obtained by moisture presoaking before impregnation of the monomer. Increases in molecular weight as well as in the number of both grafted branches were observed with increase in ΔL_{H_2O} up to ca. 4% in the lower range of ΔL_{H_2O} . However, for the number of polymer branches grafted to holocellulose, the increase reached a peak at ΔL_{H_2O} of ca. 4%, in contrast to the continuous increase of both molecular weights \bar{M}_n and \bar{M}_w . This is due to the bimolecular recombination-type termination of the propagating radicals mutually between those originating from the holocellulose and the irradiated MMA within the cellular parts or due to their termination onto lignin. The polymer branches grafted to lignin came from the latter termination, and it was found that the lower molecular weight branches grafted to lignin came from those propagating radicals which were produced from irradiated MMA in the void space and terminating onto lignin.

INTRODUCTION

As reported previously,^{1,2} only polymer grafted to the cellular parts of wood can improve its dimensional stability by reducing moisture adsorption. Therefore, the objective of the present study is to characterize the polymers by clarifying their places of origin in the wood (void space, holocellulose, and lignin), their yield, and their molecular weights. On the basis of these data, the number of polymer branches grafted to each of them can be calculated.

A large number of studies have been pursued so far on various topics in wood-polymer composites (WPC). The majority of the studies are concerned with WPC systems produced by γ -ray irradiation or heat catalyst methods, while there are only a few studies on electron beam irradiation. Samples with good polymer yield can be prepared by γ -ray irradiation regardless of the thickness of the samples. Because of the presence of the depth-dose relationship, the electron beam method limits the shape of the products. However, its strong dose rate favors the quick polymerization in particular cases such as in strengthening the property of thin fancy surfaces and the core veneers of laminated products separately by electron curing or as in the case of surface coating curing of the vanish. Although several studies have been published on the isolation of polymer from WPC by γ -ray irradiation^{3,4} or by heat catalysts⁵ and on the dependence of the molecular weights of the homopolymer on total dose,⁶ only a few studies

have been carried out so far on the isolation of such polymers prepared by electron beam irradiation. The details of their mechanism of polymerization in the respective parts of wood have not yet been clarified. It was recognized previously^{2,7} that polymers were hardly produced in the void spaces of wood by electron beam irradiation when the monomers were immersed in dry wood. However, monomers were polymerized in the cellular parts under electron beam irradiation when immersed in preswollen wood. This was due to the following reasons: The excess number of irradiated radicals was formed by the relative high dose rate of each shot of electron beams for the liquid monomers stored in the voids as compared to the dispersed ones within the cellular parts. Therefore, the former radicals terminated immediately forming oligomers mutually or into the propagating radicals produced within the cellular parts and creeping out through their surfaces. Hence, the present study is primarily concerned with the method of isolation of polymers grafted to holocellulose or lignin in the poly(methyl methacrylate)-WPC system which were prepared from preswollen veneers immersed in MMA by mutual irradiation. The study also deals with the changes in the number of polymer branches and their molecular weights versus the degree of preswelling, and finally with the clarification of the mechanism of graft copolymerization on the basis of the estimated number of polymer branches isolated which were attached to holocellulose or lignin.

EXPERIMENTALS

Materials

Veneers used in the study were of rotary-cut beech 0.65 mm thick which were carefully selected from factory products of similar quality. The dimension of the samples was equally adjusted to be of 10.0 cm (tangential (*T*) direction) \times 2.5 cm (longitudinal (*L*) direction) \times 0.065 cm (radial (*R*) direction). All samples were oven dried in vacuo at 80°C for 30 hr. The monomer used in the study was methyl methacrylate (MMA) which had been first treated with sodium hydroxide solution to remove the inhibitor, washed several times with water, dried, and distilled under reduced pressure.

Polymerization Process

The moisture content (M.C.) of the veneers was obtained by conditioning desiccators at a relative humidity (R.H.) of 43%, 65%, 88%, 93%, and 98%, respectively, before the impregnation of MMA. The R.H. in these desiccators had been standardized by inorganic salt solution prescribed in the literature, and the dimensional changes (ΔL_{H_2O}) were measured for preswollen veneers conditioned at each R.H. Impregnation of MMA into the preswollen veneers was followed by repeated exposure to three cycles of freezing, degassing, and thawing under vacuum. After the impregnation process, the samples were wrapped in bags made of aluminum foil, purged with nitrogen gas, sealed, and then subjected to the mutual irradiation process. Polymerization was carried out at a total dosage of 3 Mrad by a Van de Graaff-type accelerator (1.5 MeV voltage and 30 μ A amperage). After these processes, the residual monomer in the system was removed by vacuo at room temperature for ca. 5 hr and the termination was com-

pleted by heating at 80°C for 30 hr. For the particular case of completing the termination of the residual radicals by postpolymerization, the irradiation samples were directly heated at 80°C for 30 hr. ΔL_{H_2O} was measured primarily in the T direction. The following relationships are given for the dimensional change (ΔL_{H_2O}), the moisture content (M.C.) induced by moisture presoaking before impregnation of MMA, and the polymer content (P.C.):

$$\Delta L_{H_2O} (\%) = \frac{L_{H_2O}}{L_0} \times 100$$

$$\text{M.C.} = \frac{W_{H_2O}}{W_0} \times 100$$

$$\text{P.C.} = \frac{W_{\text{polymer}}}{W_0} \times 100$$

where L_0 is the length of oven-dried wood along the T direction, L_{H_2O} is the elongation in the T -direction induced by moisture after presoaking at various relative humidities, W_0 is the weight of oven-dried wood, W_{H_2O} is the weight of moisture in the presoaked system, and W_{polymer} is the weight of the polymer.

Electron Spin Resonance Spectra

ESR spectra of the wood were measured with a Model JES-3BSZ-type ESR spectrometer by Japan Electron Optics Laboratory operating at 100 kHz field modulation.

Isolation of Polymer from Wood

Homopolymer and grafted polymer were isolated from the WPC system in the order of homopolymer, polymer branches grafted onto holocellulose and those grafted onto lignin successively by the procedures shown in Figure 1. First, the irradiated samples were chopped into 3 mm \times 3 mm pieces, and these pieces were pulverized to below 35 mesh by grinding. Second, the homopolymer was removed by Soxhlet extraction with benzene. Third, the polymer branches grafted to holocellulose were isolated and removed from the system by complete hydrolysis of holocellulose using the hydrochloric acid method.⁸ The details of

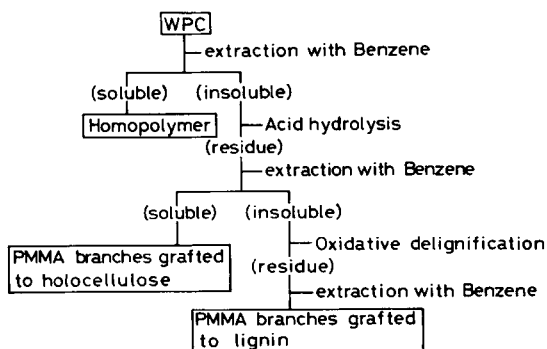


Fig. 1. Isolation method of PMMA homopolymer and PMMA branches grafted to holocellulose or to lignin from PMMA-WPC system.

this isolation process were as follows: After removing homopolymer by Soxhlet extraction for 30 hr, the extracted residue was oven dried. Then hydrochloric acid ($\rho = 1.225$) was added in the ratio of ca. 100 ml per 1 g wood and the mixture was stirred slowly for 25 hr at room temperature. After the addition of cold water by floating lumps of ice, the reaction vessel was left to stand overnight and the mixture was then filtered. After 5% sulfuric acid was added to the residue in the ratio of 100 ml per 1 g wood, the system was refluxed under heating for 6 hr and the insoluble portion was filtered off. After washing, drying, and another Soxhlet extraction, the polymer branches considered to be grafted to holocellulose were obtained. Since PMMA is stable to oxidation by chlorous acid,⁹ polymer branches grafted to lignin could be isolated successively by decomposing the residual lignin parts using the chlorite method.^{10,11} The details of this procedure were as follows: After removing the polymer branches considered to be grafted to holocellulose, ca. 0.1 ml acetic acid per 1 g wood and ca. 0.3 g sodium chlorite per 1 g wood were added to the extraction residue respectively. Then the system was heated at 70–80°C for 1 hr. Then, another 0.1 ml of acetic acid and ca. 0.3 g sodium chlorite were added to the system per 1 g of wood. The heating was continued at 70–80°C for another 1 hr. After a total of four times of chloriting, the reactant was filtered off, washed with cold water, and then dried. Finally, the polymer branches considered to be grafted to lignin were obtained by Soxhlet extraction. Degradation of PMMA did not occur during the hydrolysis and delignification processes, judging from the evidence of separate experiments that the same molecular weight distribution and the same infrared spectra were obtained before and after the treatment using standard PMMA. Besides, there was no indication of any glucosidic adsorption in the infrared spectra of grafted PMMA branches, indicating that almost pure polymer branches without any long tails of glucosidic linkages were isolated from the grafted product. The total yield of isolated polymers was 90–100% based on the total polymer content after irradiation.

Determination of Molecular Weight Distribution of Isolated Polymers

The molecular weight distributions of homopolymer and polymer branches grafted to holocellulose and to lignin were determined using a model 200-type GPC by Waters Associates using columns of 8.5×10^3 , 1×10^3 , 3×10^3 – 7×10^2 , 3.5×10^2 – 1.5×10^2 , and 0.8×10^2 – 0.5×10^2 Å with tetrahydrofuran as the eluting solvent. For polymers isolated from the sample by postpolymerization, 3×10^6 , 1×10^5 , 8.5×10^3 , and 3×10^3 – 7×10^2 Å columns were used. The sample concentration was ca. 0.2%, injection time was 120 sec, and the flow rate was 1 ml/min at an operating temperature of 40°C. Polystyrenes of very narrow molecular weight distribution were used to standardize the calibration curve of molecular weight for PMMA versus elution numbers according to the method of Huang et al.¹²

RESULTS AND DISCUSSION

As reported previously,⁷ the preswollen state of wood due to moisture pre-soaking is concerned with MMA conversion (%) to PMMA, and hence the mode of the polymerization of MMA under mutual irradiation is presumed to be

governed primarily by the impregnated amounts of monomers in the swollen cellular parts similar to other systems such as poly(vinyl alcohol),¹³ cellulose,¹⁴⁻¹⁸ and starch.¹⁹ However, the polymerization of MMA in wood could not be achieved by the preirradiation process using MMA-methanol-water (20-60-20%) as the reactant system. It is suggested that even though the swelling of irradiated wood is induced by the polar solvent of the reactant system, the quenching of the radiation-induced radicals by water precedes the formation of the propagating radicals. The presence of MMA propagating radicals and their attenuation representing the growth of grafted polymers were not recognized in the ESR patterns. As shown in Figure 2, only the surviving portion of radiation induced wood radicals could still be observed even after the soaking of the irradiated samples in water which probably existed deep in the cellulose crystallites of wood.

As illustrated in Figure 3, the augmentation in polymer content (P.C.) is observed versus the increase in ΔL_{H_2O} regarding polymer branches removed from the system which were grafted to holocellulose, lignin, and homopolymer, respectively. A higher value of ΔL_{H_2O} is indicated for the delayed initiation of the increase in the plot of P.C. of the polymer branches grafted in lignin versus ΔL_{H_2O} .

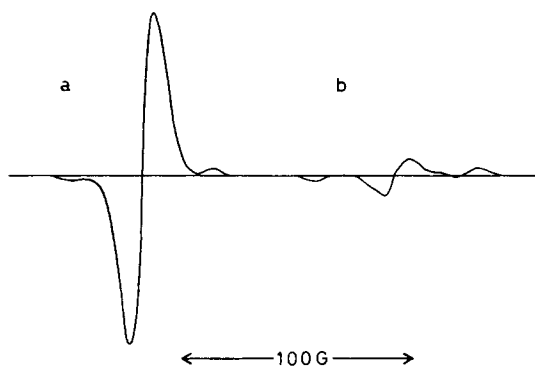


Fig. 2. ESR patterns of irradiated wood: (a) dry state; (b) after soaking in water.

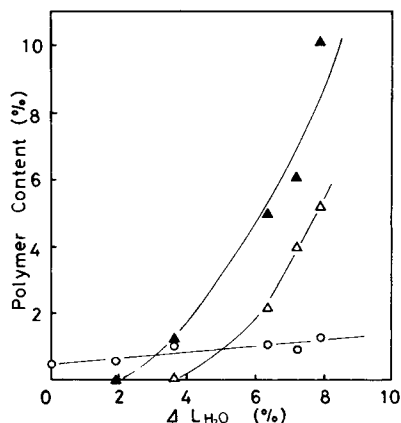


Fig. 3. Effect of dimensional change from swelling by presoaking in water (ΔL_{H_2O}) on polymer content of isolated polymers. (O) homopolymer; (▲) polymer branches grafted to holocellulose; (△) polymer branches grafted to lignin.

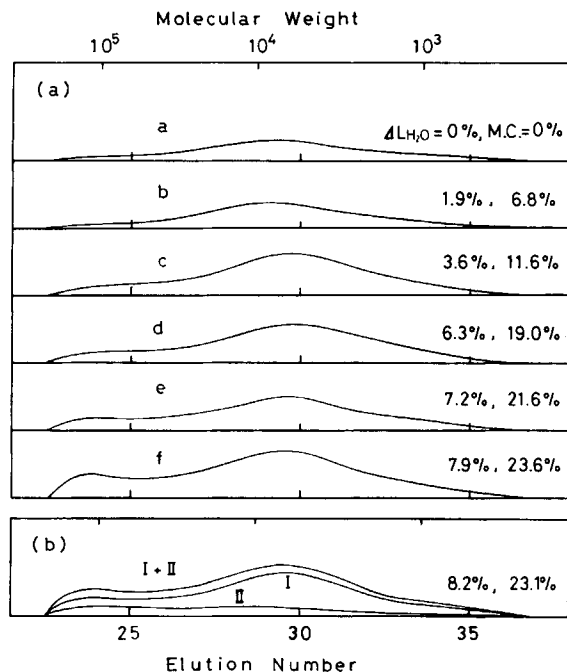


Fig. 4. (a) Effect of ΔL_{H_2O} on GPC patterns of homopolymer. (b) GPC patterns of homopolymer separated into two parts from presoaked wood-polymer composite (WPC) at ΔL_{H_2O} of 8.2%: I, isolated from veneer WPC; II, succeedingly isolated from pulverized WPC.

when compared to the indicated value of ΔL_{H_2O} for the initiation of the increase in the P.C. of polymer branches grafted to holocellulose versus ΔL_{H_2O} . However, only a small increase is observed versus ΔL_{H_2O} for P.C. of the homopolymer, indicating an accompanying increase in the molecular weight distribution of the high molecular weight fractions, as shown in Figure 4. It should be mentioned that the areas representing the weight of the corresponding fractions in Figure 4 are normalized by the homopolymer P.C. in Figure 3. This may be due to the increase in the frequency of inducing radical transfers from the cellular part to the monomer in the void space. There is a correlation between the augmentation in both P.C. and the increase in the mean molecular weight versus ΔL_{H_2O} regarding the polymer branches grafted to holocellulose and lignin in Figures 5 and 6, respectively. It should also be mentioned that the areas representing the weight of the corresponding fractions in both figures are normalized by the P.C. in Figure 3. Regarding the molecular weight distribution of homopolymer, Figure 4(a) shows that the distribution patterns of homopolymer do not change compared to those in the presoaked moisture content, showing equal peaks at ca. 6.7×10^3 . They exhibit an equally wide distribution, and the highest fraction in their molecular weight distribution is 2×10^5 . This suggests the multiplicity in the formation mechanism of the homopolymer partly due to the contribution of the effect of the postpolymerization of the induced radicals of each shot in the mutual irradiation as the total dosage increases. In order to exemplify the complexity of the kind of homopolymers thus produced in the microvoids and the interfaces, the homopolymers were isolated alternatively by two different methods. Homopolymer I was extracted directly from veneer-shaped wood-

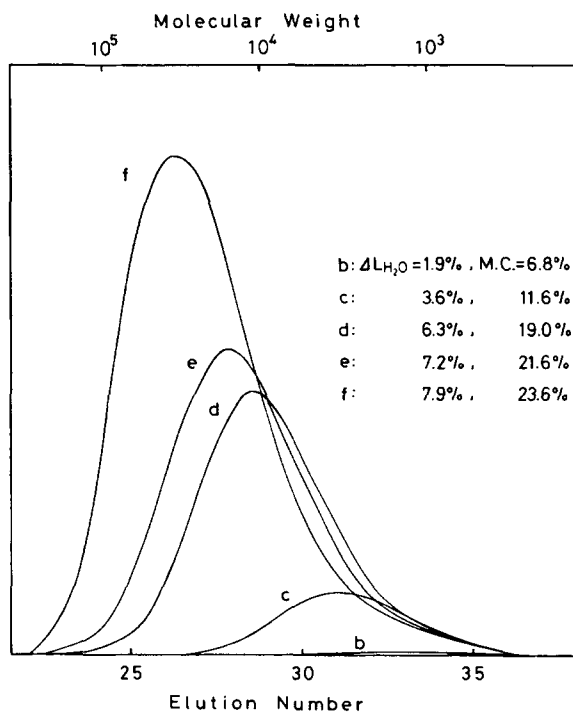


Fig. 5. Effect of ΔL_{H_2O} on GPC patterns of polymer branches grafted to holocellulose.

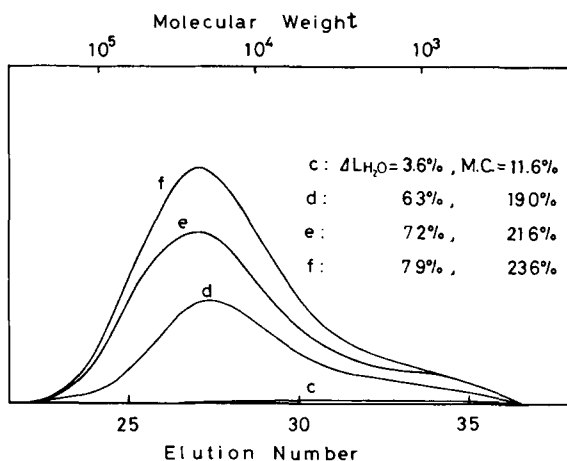


Fig. 6. Effect of ΔL_{H_2O} on GPC patterns of polymer branches grafted to lignin.

polymer composite (WPC) prepared at ΔL_{H_2O} of 8.2%. Then, the sample was chopped into fine pieces and pulverized, from which homopolymer II was obtained by subsequent extraction. The molecular weight distribution patterns of homopolymers I and II are shown in Figure 4(b). Regarding the molecular weight distribution of homopolymer I, a peak was observed at 6.7×10^3 , while homopolymer II illustrates a wide distribution with its peak at ca. 1.4×10^4 . The distribution pattern derived as the sum of the distributions of homopolymers II and I seems likely to coincide with the one (f) of the homopolymer from the originally pulverized samples in Figure 4(a). The molecular weight distribution

of homopolymer I lacks the higher molecular weight as compared to the one (f) originally from the pulverized sample. This means that most parts of the homopolymer come from the bimolecular recombination termination of excess propagated radicals produced from irradiated MMA monomer-rich microvoids, and hence their molecular weight should be low. The relatively greater weight ratio of higher molecular weight fractions in homopolymer II probably comes from the large molecular weight polymer grown close underneath the surface of the swollen cellular parts due to the autoacceleration or a gel effect which prevents the termination. Figure 5 shows the molecular weight distribution patterns of the isolated polymer branches considered as grafted to holocellulose. The molecular weight of the polymer branches grafted to holocellulose grows with the increase in the presoaked M.C., showing a shift of the distribution peak covering the molecular weight range from ca. 3.2×10^3 at $\Delta L_{H_2O} = 3.6\%$ up to ca. 3.9×10^4 at $\Delta L_{H_2O} = 7.9\%$. The molecular weight distribution patterns of polymer branches considered to be grafted to lignin at various ΔL_{H_2O} values are illustrated in Figure 6. The molecular weight at the distribution peak rises with the increase in ΔL_{H_2O} in the lower range of presoaked moisture content below ΔL_{H_2O} of 6.3% while it does not show so much augmentation in the higher presoaked region above there.

Regarding the change in the number-average molecular weight (\bar{M}_n) and the weight-average molecular weight (\bar{M}_w) of homopolymer and polymer branches considered to be grafted to holocellulose and lignin, these are shown respectively in Figure 7 versus the increase in ΔL_{H_2O} of the moisture-pres soaked veneer before immersion of monomer. On the basis of these data, the numbers of polymer branches grafted to holocellulose and lignin per 1 g wood (\bar{N}_n, \bar{N}_w) were calculated versus the increase in ΔL_{H_2O} due to moisture presoaking and are shown in Figure 8. The molecular weight of the polymer branches grafted to holocel-

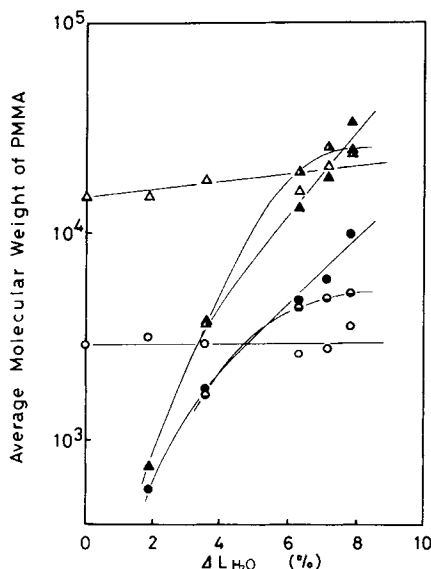


Fig. 7. Effect of ΔL_{H_2O} on number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_w) of isolated polymers: (○) \bar{M}_n ; (△) \bar{M}_w , homopolymer; (●) \bar{M}_n ; (▲) \bar{M}_w , polymer branches grafted to holocellulose; (◐) \bar{M}_n ; (◑) \bar{M}_w , polymer branches grafted to lignin.

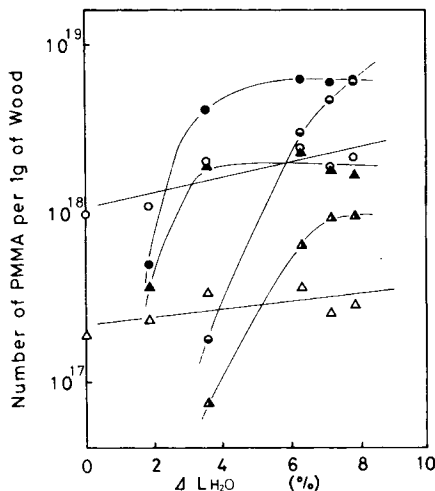


Fig. 8. Effect of ΔL_{H_2O} on the number of isolated polymers per 1 g wood: (O) \bar{N}_n ; (Δ) \bar{N}_w , homopolymer; (●) \bar{N}_n ; (\blacktriangle) \bar{N}_w , polymer branches grafted to holocellulose; (\ominus) \bar{N}_n ; (\blacktriangle) \bar{N}_w , polymer branches grafted to lignin.

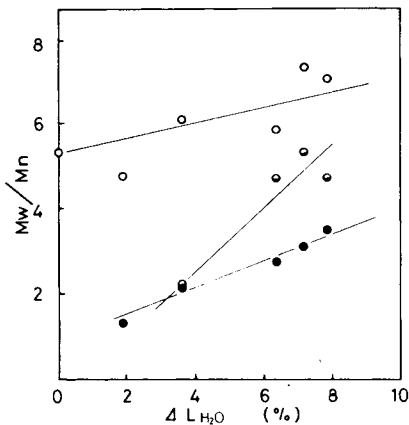


Fig. 9. Effect of ΔL_{H_2O} on the polydispersity ratio (\bar{M}_w/\bar{M}_n) of isolated polymers: (O) homopolymer; (●) polymer branches grafted to holocellulose; (\ominus) polymer branches grafted to lignin.

lulose increases versus ΔL_{H_2O} with increase in their number in the lower range of ΔL_{H_2O} up to ca. 4%, where the increase of the latter stops. However, the increase of the former still continues. On the other hand, the increase in both molecular weights (\bar{M}_n , \bar{M}_w) of the polymer branches grafted to lignin and the number (\bar{N}_w) calculated from \bar{M}_w , are recognized versus the increase in ΔL_{H_2O} up to ca. 6%, while the promotion in the number (\bar{N}_n) calculated from \bar{M}_n is still continued above a ΔL_{H_2O} of ca. 6%. As for the homopolymer, smaller increases regarding the molecular weight and the number of polymer chains are observed, illustrating the relative gain in higher molecular weight fractions. This evidence endorses our understanding of the pattern on the polymerization mechanism: On immersion of the preswollen veneer into MMA, MMA molecules dwell primarily within the void space. During repetition of the freeze and thaw operations, MMA molecules gradually move to the swollen cellular parts by replacing adsorbed moisture without any change in the elongated length by the stripping

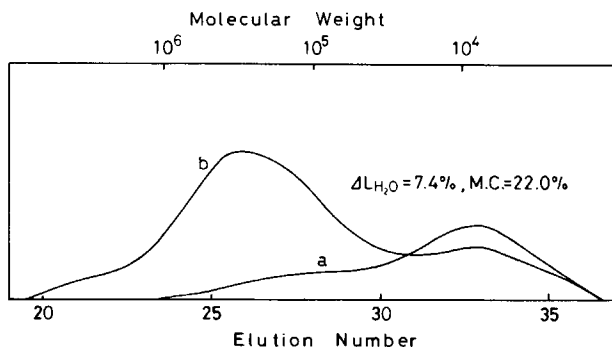


Fig. 10. Effect of postpolymerization on GPC patterns of homopolymer: (a) control; (b) post-polymerization.

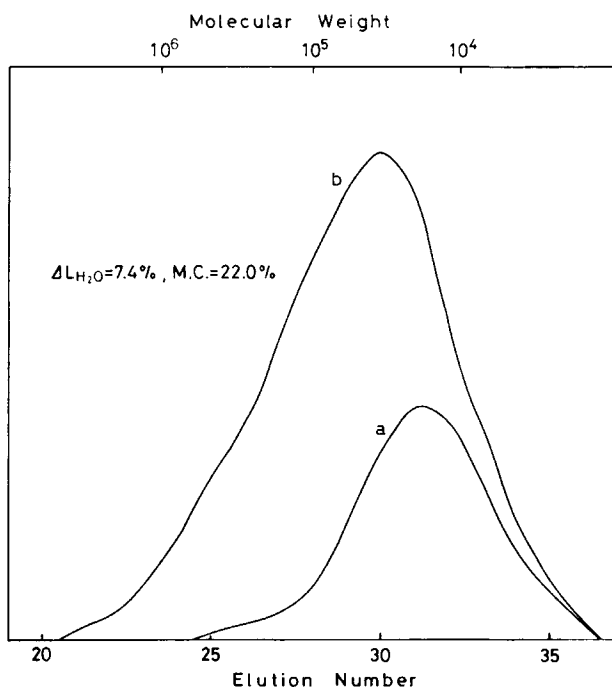


Fig. 11. Effect of postpolymerization on GPC patterns of polymer branches grafted to holocellulose: (a) control; (b) postpolymerization.

of the moisture. Therefore, some MMA parts are distributed in the swollen cellular parts and the rest are distributed in the void space after the operation. The distribution ratio must depend on the initial elongated length of the veneer. Thus, the number of MMA monomers in the preswollen cellular parts and those in the void space was proportional to ΔL_{H_2O} . In addition, it was previously reported⁷ that the conversion was found to be proportional to the root of the dosage at a definite ΔL_{H_2O} and the monomers were hardly polymerized in the void space under electron beam irradiation by the Van de Graaff-type accelerator. The length of the preswollen veneer immersed in MMA is further elongated at each shot of irradiation regardless of the fact that the volume of the liquid MMA is itself contracted on polymerization. Quick polymerization must occur among

irradiated radicals probably on the CH_2OH groups of holocellulose and among irradiated MMA radicals. Hence, it can be presumed that the moisture solubilized in MMA or adsorbed on the CH_2OH groups is stripped off during polymerization and moves to the perturbed parts due to the strain of the polymerized polymers and also to the heat of polymerization evolved there. The perturbation of the rigid parts by the strain of the produced polymers is suggested by the evidence of the dielectric study for the PMMA-WPC system, indicating a lowering of the activation energy of the rotational motion of the CH_2OH groups and the nonuniformity in the distribution of the relaxation times.²⁰ The transferred moisture swells the system under the gradual transport of MMA there during the interval for the next shot. During the next irradiation shot, these monomer are polymerized and the polymerized polymers again elongate the dimension of the system to invite another intrusion of moisture. The number of the induced propagating radicals is presumed to be proportional to the amount of MMA residing in each channel along the amorphous regions of the cellulose fibril structure. The polymerization proceeds under the repeated irradiations within each channel in the semiloosened structure of the swollen cellular parts below a $\Delta L_{\text{H}_2\text{O}}$ of ca. 4%. This results in the formation of the propagating radicals either from the radiation-induced wood radicals or from the irradiated MMA in proportion to the immersed MMA in the system. Most of the latter are expected to be terminated by mutual recombination within the swollen cellular parts on the basis of the results as obtained from GPC patterns. However, the surviving ones will reach the surface of the swollen cellular parts, and most of them are probably terminated with the phenolic inhibiting ingredient^{21,22} of the lignin, the probability depending on the random motion of the polymer chains. Herewith, it is proposed that these inhibiting ingredients are preliminarily exposed on the surface of the cellular parts by swelling. The rest creep out onto the void space, crossing through the surface, and are terminated by the recombination with these propagating radicals produced from the irradiated MMA in the void space.

It should be mentioned that the foregoing discussion on the mechanism of radiation-induced polymerization of MMA is an artificial one only based on the accumulation of facts regarding the number of polymer branches as grafted to holocellulose and lignin and their molecular weights. For the verification of the true mechanism of the graft copolymerization of MMA from irradiated wood radicals, the presence of propagating radicals of MMA compensating the irradiated wood radicals should be pursued by the change of ESR signal in terms of the preirradiation process. Because of the difficulty due to the wood complex, the mechanism under mutual irradiation seems likely to be very complex for the exact follow-up by ESR measurement. Insofar as our technique on the detection of the formation of MMA propagating radicals is concerned, there is no indication of any ESR patterns illustrating the presence of the MMA propagating radicals except the decay of wood radicals formed by the preirradiation method, as shown in Figure 2. In addition, no propagating MMA radicals were still observed under heating of the dry preirradiated wood-MMA system. Hence, it is expected that there is little possibility for a mechanism such as is observed in the grafting of MMA to preirradiated starch¹⁹ within the present precision of detecting the radicals in our measurements. This suggests that there is no graft PMMA branch from the secondary radical of wood. However, there is evidence opposing this view: The dielectric constant and the loss factor based on the rotational

motion of CH_2OH groups decrease with increase in the number of grafted polymer branches.²⁰ For the resolution of the contradictory views between the former evidence regarding the observation of the propagating MMA radical from ESR measurement and the latter evidence regarding the probability on the presence of the grafted branches onto CH_2OH groups from the dielectric loss measurement, it is suggested that under mutual irradiation the formation of propagating MMA radicals is induced only instantaneously from the CH_2OH groups on the amorphous portion of cellulose to terminate quickly with the radicals formed on the immersed MMA close to them. Therefore, we conclude that these polymer branches removed from the WPC system which are considered to be grafted to lignin by the previously mentioned isolation procedure must come mostly from those branches originating from the holocellulose parts and terminating on the lignin parts regardless of the kind of radical species. These conclusions can explain the behavior of the molecular weight and of the number of polymer branches versus $\Delta L_{\text{H}_2\text{O}}$ as shown in Figures 7 and 8. However, the \bar{N}_n of the polymer branches grafted to lignin still increase in the higher range of $\Delta L_{\text{H}_2\text{O}}$ above ca. 6%, regardless of the break in the increase of both molecular weights (\bar{M}_n, \bar{M}_w) and in the augmentation of its \bar{N}_w . Hence, it is not untrue to say that this is due to termination with the inhibiting ingredients on the widely exposed lignin layers which are spread out by the extreme swelling.

In another method of the characterization of polymers, the polydispersity ratio (\bar{M}_w/\bar{M}_n) is calculated from the data in Figure 7 of the different polymers. Figure 9 shows the change in \bar{M}_w/\bar{M}_n versus $\Delta L_{\text{H}_2\text{O}}$ for each isolated polymer. Since the increase in \bar{M}_w/\bar{M}_n of the homopolymer versus $\Delta L_{\text{H}_2\text{O}}$ is higher than that of both types of grafted chains, the multiplicity in the mode of the polymerization of homopolymer is suggested as follows: The bulk radical polymerization in monomer-rich void spaces originates from irradiated MMA, the autoacceleration polymerization occurs along the surface of the cellular parts, and the polymerization proceeds on the basis of radical transfer from the cellular parts onto the void spaces.

As for the effect of the postpolymerization at 80°C for 3 hr, an intense growth of molecular weight is observed for both homopolymer and polymer branches grafted to holocellulose as shown in Figures 10 and 11, respectively. The growth in the molecular weight of the homopolymer by postpolymerization is attributed to increase by some renewed propagation and termination at high temperature. The propagating reaction of the revived radicals is accelerated by gel effect based on the polymers which had been formed immediately after the irradiation.

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