

Impregnation of White Pine Wood with Unsaturated Polyesters to Produce Wood–Plastic Combinations

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SYNOPSIS

Two unsaturated polyester resins based on poly(1,2 propylene–maleate–phthalate) (PE1), and poly(oxy-diethylene–maleate–phthalate) (PE2) were used for the impregnation of oven-dried white pine wood samples in admixture with styrene (S). Curing was affected by the initiator-heat technique by either using 0.1–0.2% by weight of benzoyl peroxide (Bz_2O_2), or 1% by weight of methyl ethyl ketone peroxide (MEK). It was found that the use of PE1/S mixture resulted in the formation of wood–plastic combinations (wpc) with higher percent retention and higher percent polymer loadings than those obtained by the impregnation of wood samples with PE2/S mixtures. The use of different swelling solvents including ethanol, acetone or chloroform, did not influence the percent retention or polymer loadings of wpc for either PE1/S or PE2/S mixtures. Physical tests performed on wpc showed that compression, hardness, static bending were generally enhanced, water absorption was decreased, and dimensional change was retarded to different extents for both polyesters used, but no permanent stabilization was attained.

INTRODUCTION

Wood may be modified in various ways in order to change its physical,¹ chemical,² and biological properties.³ One of the techniques for altering the properties of wood that has received considerable attention in the last few years is the formation of wood–plastic combinations (wpc), by incorporating, into the wood matrix, either monomers such as styrene,⁴ methylmethacrylate,⁵ vinyl chloride,⁶ vinyl acetate,¹ mixture of different monomers,⁷ urea formaldehyde,⁸ or epoxy resin.⁹ Various types of unsaturated polyester resins have been successfully used for wood impregnation in admixture with styrene since the volatilization of the impregnating mixture is significantly reduced from the wood matrix, and wpc may be produced either by radiation^{10,11} or by thermal curing.^{12,13}

The aim of the present work is to strengthen weak-grade, low-density wood by impregnating several samples of white pine wood with two kinds of unsaturated polyester resins. The physicomechanical properties of the resulting wpc are studied, and

the effect of polyester composition on such properties is also discussed. The final goal is improving dimensional stability, reducing water absorption, increasing bending, hardness, and compression strength.

EXPERIMENTAL

Wood Samples

Samples of as high homogeneity as possible of white pine were chosen from several defect-free boards of pine wood. They were cut into blocks of $2 \times 2 \times 3$ cm for measurements of hardness, compression, water absorption, and dimensional change, and into blocks of $1 \times 1 \times 15$ cm for measurements of static bending. The surface was smoothed carefully to avoid blocking of the pores.

Polyester Resins

1-Polyester (PE1) was a commercially obtained, all-purpose polyester, manufactured by Eternal Chem. Co. Ltd., containing 1,2-propylene glycol, maleic anhydride, and phthalic anhydride and having about 37–39% of styrene and a viscosity of 450 cps. It was

diluted with styrene (S) up to 50% for the impregnation process. Curing was affected either by 0.2 wt % benzoyl peroxide (Bz_2O_2) or with 1 wt % methyl ethyl ketone peroxide (MEK).

2-Polyester (PE2) was prepared and purified following the procedure reported,¹⁴ by the polycondensation of diethylene glycol (1 mol), maleic anhydride (0.5 mol), and phthalic anhydride (0.5 mol). It was used with styrene monomer (30 wt %) (Fluka A. G. Chemische Fabrik, CH-9470-Buchs) for the impregnation process and cured with 0.1 wt % Bz_2O_2 .

Impregnation Technique

Without Swelling Agents

The wood samples (density 0.454 at approximately 9% moisture content) were oven-dried at 105°C for 4 h. They were placed in a desiccator and held under reduced pressure for 0.5 h. The desiccator was then flooded with sufficient (PE/S) mixture from a dropping funnel to completely immerse the wood samples. The system was then vented to atmospheric pressure and the samples were allowed to soak for further 2 h to ensure maximum (PE/S) mixture uptake. The wood samples were then air-dried and weighed. Curing was then affected at 60°C for 24 h, at 80°C for 2 h, and finally at 105°C for 2 h to ensure maximum crosslinking. They were then put in a desiccator under vacuum for 0.5 h to ensure removal of uncured products. Several crushed impregnated wood samples were soaked in chloroform for 1 week with frequent shaking. The mixture was then filtered and the wood samples were oven-dried at 80°C for 4 h in order to remove any homopolymer formed. Percent crosslinking was then estimated.

Using Swelling Agents

The oven-dried, weighed wood samples were soaked in either ethanol, acetone, or chloroform for 24 h. The samples were then dried at 60°C for 4 h and the impregnation technique cited in (A) was followed with the two PE/S mixtures.

Measurements

The following values were obtained:

$$\% \text{ PE/S retention } (R) = \frac{W_1 - W_0}{W_0} \times 100$$

$$\% \text{ polymer loading } (L) = \frac{W_2 - W_0}{W_0} \times 100$$

$$\% \text{ conversion} = \frac{L}{R} \times 100$$

$$\% \text{ crosslinking} = \left(1 - \frac{W_1 - W_3}{W_1} \right) \times 100$$

$$\% \text{ total volumetric swelling } (S)^{15} = \frac{V_1 - V_0}{V_0} \times 100$$

$$\% \text{ antiswell efficiency } (ASE)^{15} = \frac{S - S_1}{S} \times 100$$

where W_0 and W_1 are oven-dry weights of wood samples before and after impregnation, W_2 is the weight of wpc after curing, W_3 is the weight of wpc after soaking in chloroform, V_0 and V_1 are the total volumes of untreated and treated wood samples, and S and S_1 are the percent total swellings before and after treatment, respectively.

Water Absorption and Dimensional Change

Specimens of $2 \times 2 \times 3$ cm were used for this study. Treated and untreated samples were oven-dried at 60°C for 4 h, and then submerged in water for varying lengths of time. At the end of each time interval, the samples were slowly air-dried in order to minimize drying defects. The percent water absorbed, percent volumetric swelling coefficient, and the ASE were calculated.

Compression Parallel to Grain

Specimens for compression test were $2 \times 2 \times 3$ cm in dimensions. They were tested in accordance with the procedures of ES-650-1965.¹⁶

Hardness

The procedures of ES-650-1965¹⁶ (the ball-penetration method) were followed on samples of $2 \times 2 \times 3$ cm in dimensions.

Static Bending

Wood samples of dimensions $1 \times 1 \times 15$ cm were used for this test in accordance with the procedure of ES-650-1965.¹⁶

RESULTS AND DISCUSSION

Effect of Swelling Agent, Polyester Structure and Initiator Type on Percent Retention (R) and Percent Polymer Loading (L) of wpc

Data in Table I indicated that, generally, the use of either ethanol, acetone, or chloroform as the swelling solvent did not affect the percent retention R of PE/S mixtures in the wood samples impregnated as

Table I Effect of Swelling Agents, Polyester Structure and Initiator Type on Percent Retention (*R*), Polymer Loading (*L*), and Percent Conversion of wpc

Polyester	Initiator	Swelling Agent	% Retention <i>R</i>	% Polymer Loading <i>L</i>	% Conversion <i>L/R</i>	% Crosslinking
PE1	Bz ₂ O ₂	—	102.2	95	92.9	91.2
PE1	Bz ₂ O ₂	Ethanol	99.4	97	97.6	
PE1	Bz ₂ O ₂	Acetone	84	76.8	91.4	
PE1	Bz ₂ O ₂	Chloroform	93	92	98.9	
PE1	MEK	—	79.3	72	90.8	84.9
PE1	MEK	Ethanol	70.5	65	92.2	
PE1	MEK	Acetone	79	76.8	97.2	
PE1	MEK	Chloroform	69.2	66	95.4	
PE2	Bz ₂ O ₂	—	121.8	115	94.4	84.4
PE2	Bz ₂ O ₂	Ethanol	118	110	93.2	
PE2	Bz ₂ O ₂	Acetone	139.7	120	85.9	
PE2	Bz ₂ O ₂	Chloroform	119.7	109.5	91.5	

compared to samples impregnated without any swelling solvents. Table I also revealed that when Bz₂O₂ was used as the initiator, *R* for wood samples impregnated with PE2/S mixture, was higher (119–140%) than *R* for wood samples impregnated with PE1/S mixtures (80–100%). Although this may be due to variation in the uniformity of distribution of wood constituents from one test piece to the other, it may also be accounted for as postulated by Callerton et al.⁶ by assuming that PE2, with a diethylene glycol residue in its backbone structure, had a closer similarity to wood structure, and hence passed more readily into wood samples as compared with PE1 with a 1,2-propylene glycol residue in its backbone structure.

Close inspection of Table I also revealed that the use of Bz₂O₂ as the initiator in the impregnation of wood samples by PE/S mixture resulted in higher percent retention *R* by wood samples as compared with MEK when used as the initiator for the impregnation of wood samples with the same polyester. This may be due to the fact that the crosslinking rate of polyester PE1 and styrene was faster with MEK as the initiator than with Bz₂O₂ and hence the viscosity of the impregnating mixture was increased resulting in lower *R* by wood samples. Such an effect has been observed by Kawarkami et al.¹⁷ Table I showed that high percent polymer loading (*L*), high percent conversion, and high percent crosslinking of PE/S were obtained for all wpc

Table II Water Absorption and Volumetric Antiswell Efficiency (ASE) of wpc

Polyester	Initiator	Average Polymer Loading (%)	No. of Days	Water Absorbed (wt %)	Volumetric Swelling Coefficient (%)	ASE (%)
—	—	—	1	51.2	13.2	—
—	—	—	7	78.9	14.9	—
—	—	—	14	107.5	11.4	—
—	—	—	21	117.1	11.4	—
PE1	Bz ₂ O ₂	—	1	16.2	5.0	62.1
PE1	Bz ₂ O ₂	78.8	7	29.2	10.4	30.2
PE1	Bz ₂ O ₂	—	14	34.1	7.0	38.6
PE1	Bz ₂ O ₂	—	21	35.9	7.0	38.6
PE1	MEK	—	1	7.5	5.0	62.6
PE1	MEK	68.8	7	20.9	8.3	44.3
PE1	MEK	—	14	28.9	6.6	42.1
PE1	MEK	—	21	31.9	6.6	42.1
PE2	Bz ₂ O ₂	—	1	16.7	7.8	40.9
PE2	Bz ₂ O ₂	94.4	7	29.9	11.3	24.2
PE2	Bz ₂ O ₂	—	14	39.2	10.4	8.8
PE2	Bz ₂ O ₂	—	21	41.5	10.4	8.8

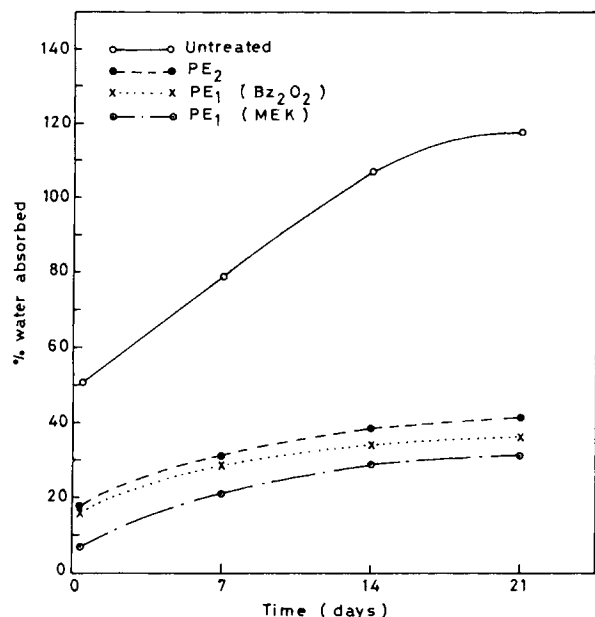


Figure 1 Effect of soaking time on percent water absorption of WPC compared to untreated wood.

formed with either (PE1/S) or PE2/S mixtures. This indicated high efficiency in the degree of cross-linking reaction of polyester with styrene monomer in the wood samples.

Water Absorption and Antiswell Efficiency of wpc

Data for percent water absorption, volumetric swelling coefficient, and antiswell efficiency shown by wpc during immersion in water for 3 weeks are

shown in Table II and Figures 1 and 2. Results showed that the percent water absorbed was greatly retarded after 3 weeks in wpc formed by the impregnation of either types of the investigated (PE/S) mixtures, as compared to untreated controls. The effect was most pronounced with wpc formed with PE1(MEK)/S mixture, in spite of their average lower polymer loading (L) (68.8%), as compared with PE1(Bz₂O₂)/S wpc (78.8%) or (PE2/S) wpc (94.4%). This result clearly suggested that the uptake of water by wpc was affected not only by the structure of polyester resin used, but also by the type of initiator used for curing, a factor which could have affected the distribution of crosslinked polymer in wood structure.¹⁸

It was also apparent from Table II that the percent volumetric swelling (S) was also reduced for all wpc as compared with untreated controls. It is worth mentioning that the maximum percent swelling (S) was attained after seven days of soaking for all wpc tested.

ASE values for wpc were found to be time dependent (Table II and Fig. 2). In the order of decreasing stability, the three types of wpc showed the following: after 24 h of soaking, PE1 (MEK/S) wpc (ASE 62.6%), almost similar to PE1 (Bz₂O₂/S) wpc (ASE 62.1%) followed by (PE2/S) wpc (ASE 40.9%).

After 3 weeks of soaking, the average ASEs were 42.1, 38.6, and 81.8% for PE1 (MEK), PE1 (Bz₂O₂), and PE2/S mixtures, respectively. Hence the ASE of the wpc investigated would probably become zero with time, and no permanent stability would be obtained. These results are quite in agreement with

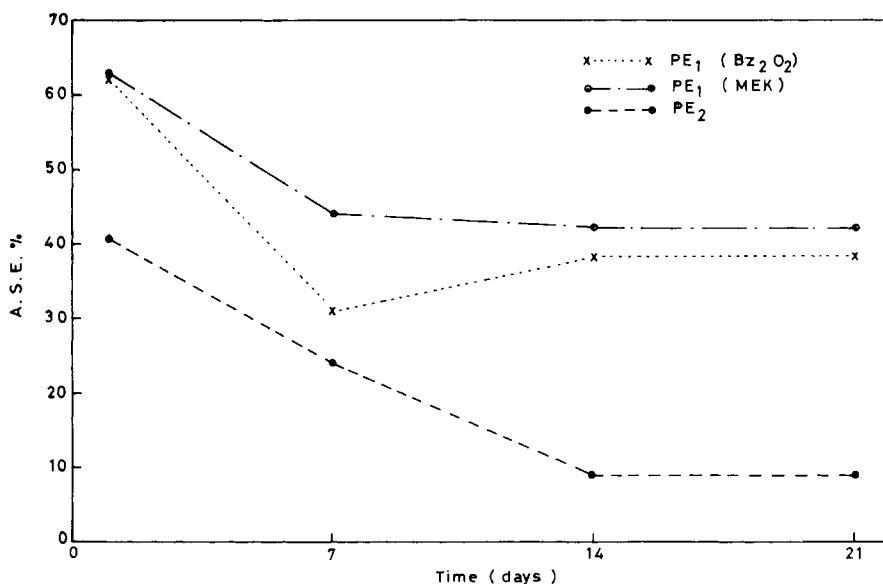


Figure 2 Effect of soaking time on percent volumetric antiswell efficiency of various WPC.

those reported by Calleton⁶ and may also be rationalized by assuming that, during the impregnation process, polyesters do not bulk the cell walls, but add weight in wood lumens and hence do not result in dimensional stability to any great extent.

Compressive Strength of wpc

Data for compressive strength parallel to the grain of white pine wpc as compared to untreated controls are illustrated in Figure 3. Results shown were the average of 10 test runs in each case. Samples of comparable percent polymer loadings were chosen for this test. It is quite evident from Figure 3 that the use of either (PE1/S) or (PE2/S) for the impregnation process, resulted in wpc with enhanced compressive strength values, as compared with untreated controls. Highest values were observed with PE1 (Bz_2O_2) which exhibited about twice the values of compressive strength as those for untreated wood samples (Fig. 3). The smallest values for compressive strength were obtained with (PE2/S) mixtures. Such results clearly demonstrated the effect of polyester structure on the compressive strength of wpc.

Hardness of wpc

Data in Figure 4 for the hardness of wpc illustrated that the incorporation of either (PE1/S) or (PE2/S) mixtures into wood structure to form wpc resulted in an increase in hardness values of all wpc

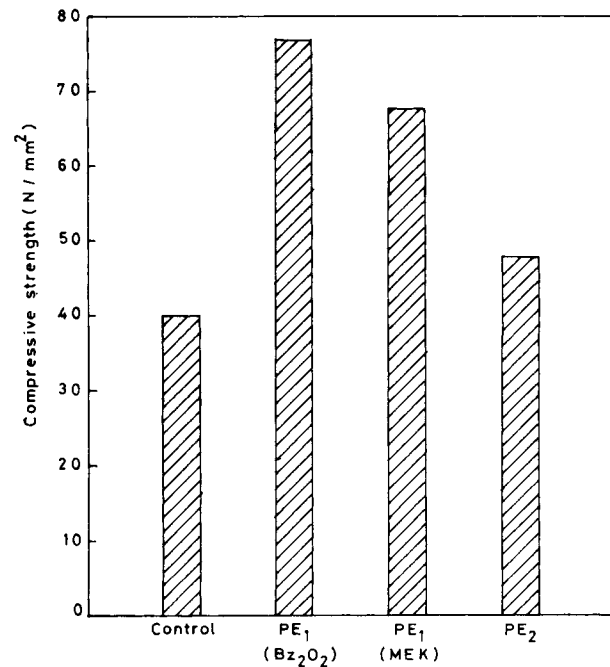


Figure 3 Compression of white pine composites compared to untreated controls average of 10 samples.

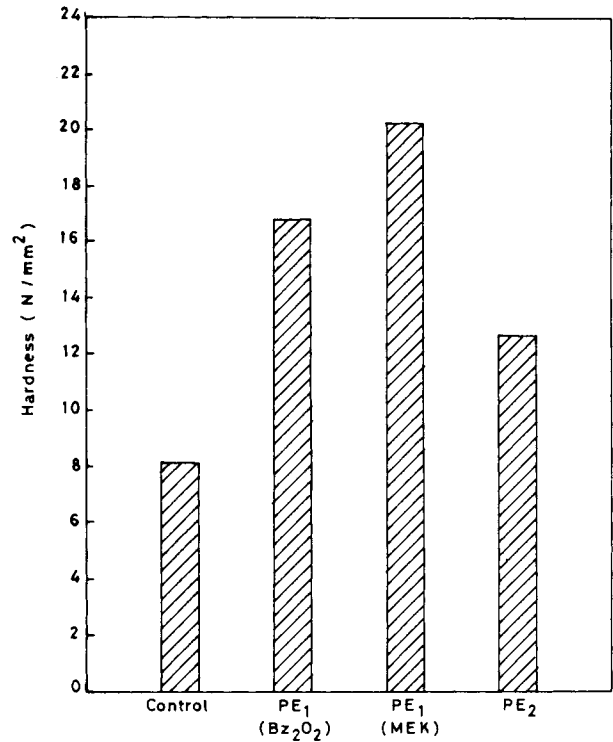


Figure 4 Hardness of white pines composites compared to untreated controls average of 10 samples.

over that of untreated controls. Using wpc with comparable polymer loading, it may be seen from Figure 4 that the highest values for hardness were obtained with wpc formed with PE1/S mixtures,

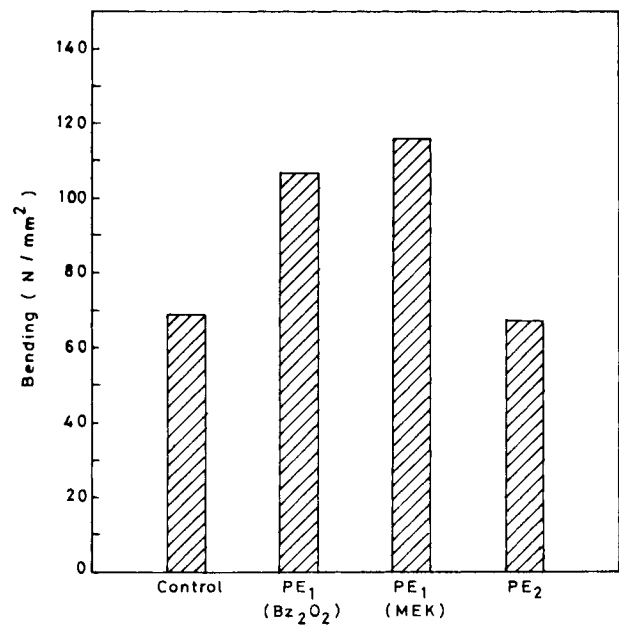


Figure 5 Bending of white pine composites compared with untreated controls average of 10 samples.

followed by wpc formed with PE1(Bz₂O₂)/S mixtures and the lowest values were obtained with wpc formed with PE2/S mixtures.

Static Bending of wpc

Data for static bending of wpc are included in Figure 5. Data shown were the average of 10 test runs in each case. WPCs with comparable polymer loading values were chosen. It is clear that although the incorporation of PE1(Bz₂O₂)/S mixtures or PE1(MEK)/S mixtures into wpc resulted in substantial increase in static bending values, the use of PE2/S mixtures for impregnation did not lead to any increase in static bending values of the formed wpc. This test clearly demonstrated that the type of polyester played an important role in determining the mechanical properties of the formed wpc.

CONCLUSION

From this study, the following conclusions were drawn:

1. The impregnation of white pine wood with two different types of polyesters resulted in wpc with generally enhanced physical properties.
2. The type of initiator used for crosslinking greatly affected the percent polymer loadings and the physical properties of the formed wpc.
3. The use of poly(1,2-propylene-maleate-phthalate) (PE1) as the impregnating mixture with styrene resulted in wpc with more enhanced physical properties than those formed with PE2 based on poly(oxy-diethylene-maleate-phthalate).
4. Permanent dimensional stabilization with any one of polyesters used for impregnation was not attained with vacuum pressure method since the average ASE values were found to be function of time.
5. Values for compression and hardness of wpc were increased to different extents for all polyesters used, whereas the static bending

values increased only with (PE1/S) wpc and no increase was observed with (PE2/S) wpc.

REFERENCES

1. J. A. Kent, A. Winston, W. Boyl, and L. Updyke, in *Proceedings of the Conference on the Application of Larger Radiation Sources in Industry*, International Atomic Energy Agency, Vienna, 1963, pp. 377-404.
2. M. H. Schneider and K. I. Brebner, *Wood Sci. Technol.*, **19**, 67-73 (1985).
3. D. Narayanamurti, M. T. Jayaramon, R. Thacker, and S. Anantanarayanan, *Wood Sci. Technol.*, **4**, 266-236 (1970).
4. E. S. A. Kandeel and M. H. Etman, *Alexandria J. Agric. Res.*, **19**, 365-373 (1971).
5. F. C. Beall and A. E. Witt, *Wood Fiber*, **4**(3), 179-184 (1972).
6. R. L. Calleton, E. T. Choong, and R. C. McIlhenny, *Wood Sci. Technol.*, **4**, 216-226 (1970).
7. A. B. Moustafa, E. E. Kandil, B. A. Hady, and N. A. Ghanem, *Angew. Makromol. Chem.*, **65**, 121-132 (1977).
8. B. I. Kupchinov, Yu. D. Baranov, and V. I. Inyutin, U.S.S.R. Pat. 733,979 (cl. B27K3134) (1980).
9. G. R. Moore, D. E. Kline, and P. R. Blankenhorn, *Wood Fiber Sci.*, **15**(3), 223-234 (1983).
10. M. Pesek, J. Jarkovsky, and F. Pultar, *Proc. Tihany Symp. Radiation Chem.*, **1**, 807-817 (1972).
11. T. Autio and J. K. Miettinen, *Forest Prod. J.*, **20**(3), 36-42 (1970).
12. J. Duran and J. A. Meyer, *Wood Sci. Technol.*, **6**, 59-66 (1972).
13. R. W. Davidson, J. A. Meyer, and C. Skaar, *Wood Sci.*, **1**(2), 116-128 (1968).
14. Composition and Utilization of Polyesters, National Aniline Division, Allied Chemical and Dye Corporation, 1954.
15. H. N. Rosen, *Wood Fiber*, **7**(4), 249-255 (1976).
16. Egyptian Standards (ES-650-1965).
17. H. Kawarkami and K. Taneda, *Rinsan Shikenzo Geppo (Hokkaido Forest Prod. Res. Inst., Jpn.)*, **10**, 22-27 (1973).
18. R. M. Rowell and W. D. Ellis, *Wood Fiber*, **10**(2), 104-111 (1978).

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