

Monomer Emulsion 에 의한 강화목재

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Wood—Polystyrene—Composite by Monomer Emulsion

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Abstract

The salient features of Luan-Polystyrene Composite using monomer emulsion, as it differs from composite using pure styrene both on the distribution of polymer in wood and mechanical behavior of products, are discussed. Wood reinforcing is achieved by loading styrene emulsion and pure styrene and by subsequent thermal polymerization. Uniformity of polymer in wood is discussed in connection with specific gravity variation, and mechanical properties are also determined. It appeared that monomer emulsion played an important role of enhancing both the uniformity and mechanical strengths.

요 약

나왕(Luan) 木材에 styrene emulsion 및 순수 styrene 單量體를 各各 침투, 重合하고 木材内部에서의 重合體의 分布거동 및 力學的 性質의 差異를 比較하였다. 強化木材化는 單量體가 침투된 木材試料를 熱重合하여 이루었고 木材内部에서의 重合體 均一分布도는 試料의 比重變化를 測定하여 검토하였다. Emulsion 을 침투, 重合한 試料에서 더 均一한 重合體의 分布가 이루어졌고 力學的 性質들도 더 우수 하였다.

Introduction

In the production of wood plastic composite there are two types of polymerization process; the radiation and thermal treatment. But it is well known that the properties of products obtained by these two methods do not show any remarkable difference. Although radiation process is advantageous in the case of large scale production, higher capital investment has turned the attention to the process involving thermal treat-

ment.

There have been also considerable attempts¹⁻³⁾ to achieve more effective impregnation of woods with hydrophobic monomers by adding swellable solvents to the impregnants. Ross et al.⁴⁾ found that the swelling of wood with organic solvents for increasing grafting or attaining more uniform distribution of monomer caused a decrease in wood strength.

Gotoda⁵⁾ performed the impregnation of monomer emulsion to some native Swedish woods and polymerization by γ -ray irradiation to learn that the monomer

emulsion containing 0.2% of alkyl benzene sulfonate had greater reactivity and shorter induction period than in the case of methyl methacrylate-methanol solution. Also he pointed out that higher efficiency of grafting of polymer to wood could be attained by utilizing emulsion system.

Most of the experimental works, however, were limited to the evaluation of grafting efficiency of polymer to wood and finding of more effective swelling agents. Elucidations of the physical and mechanical behaviors of those products provided by addition of extra swellable solvents can hardly be found.

It is thus the purpose of the present study to prepare primarily reinforced products by thermal polymerization Luan impregnated with styrene emulsion, and to demonstrate conclusively the improved properties of the products by making comparisons with the results obtained from the bulk polymerized, on the assumption that the emulsion can induce more uniform distribution of polymers due to the powerful hydrophilic character of wood.

Experimental

1) Materials

Wood; The sapwood of Luan, $2 \times 2 \times 10$ cm along to the longitudinal direction, was pretreated to have constant moisture content at room temperature by successive steaming and drying under reduced and atmospheric pressure.

Monomer; Styrene from Wako Chemicals was vacuum distilled.

Monomer emulsion; Styrene emulsion having 62.5% of monomer content was prepared at room temperature with Tween 80 as emulsifier.

Initiators; Recrystallized benzoyl peroxide from Kawaguchi Yakuhin Co. was used for bulk polymerization whereas potassium persulfate from Kanto Chemical Co. was used for emulsion polymerization.

2) Impregnation and polymerization

Impregnation; Wood specimens, conditioned, weighed, and measured in size, were placed in a glass tube which was able to be evacuated and connected to a monomer or monomer emulsion reservoir. After the evacuation of the tube, a measured amount of

monomer or monomer emulsion was flushed in to have the specimen soaked completely. While releasing the evacuation to atmospheric pressure, specimen was kept standing for 1 min. to 12 hours.

Polymerization; After definite hours of soaking, the specimen was sealed perfectly with 0.05mm. aluminum foil. Then the sealed specimen was placed in an oven at $60 \pm 0.1^\circ\text{C}$ for 12 hours. After another hour at 100°C , the polymerized specimen was unwrapped and evacuated again until specimen revealed constant weight.

3) Measurements and calculations

Specific gravity; The apparent density of polymerized specimen was determined in terms of specific gravity according to the definition of wood physics⁶⁾.

Water absorption; Overall volume change of polymerized specimen was calculated by measuring the dimensions of specimen before and after the definite hours of soaking into water at 30°C .

Effective diffusivity; The variations of diffusion rate through the polymerized specimen along the longitudinal direction was calculated by the following equation⁷⁾. Water at $25 \pm 0.1^\circ\text{C}$ was used.

$$E = \frac{C_{A\theta} - C_{A\infty}}{C_{AO} - C_{A\infty}} = f\left(\frac{D\theta}{a^2}\right)$$

E ; The fraction immersed.

C_{AO} ; Initial water conc. in wood.

$C_{A\theta}$; Water conc. in wood at time θ .

$C_{A\infty}$; Saturated water conc. in wood.

D ; Effective diffusivity.

a ; Diffusion length of wood.

Mechanical properties; The compressive strength of specimen at lateral direction was determined according to the JIS Z 2111-63.

Indentation hardness of specimen to the radial direction was determined by the JIS Z 2117-63 except for that the inserting position of steel ball, 8.75 mm. in diameter, was fixed at the center of the specimen.

Instrument used for the determinations of mechanical properties was the universal testing machine, Instron. All the data presented were the averages of five specimens.

Results and Discussion

Since it has been found from the previous work⁸⁾ that the Lauan has shown relatively favorable behavior in loading monomers, the present work is undertaken to this wood. From the economical point of view, however, the preparations of reinforced specimens were controlled within about 50% of polymer content.

In order to visualize the degree of polymer uniformity yielded by both the emulsion and bulk polymerized specimens, the specific gravity variations of polymerized specimens along the length of a given specimen were observed. The variations of specific gravity along the polymerized specimen length have been presented in Fig. 1. From the feature that the emulsion polymerized product containing 16.7% of polymer did not exhibit any substantial changes in specific gravities along the specimen length, as shown in Fig. 1, it was manifested that the emulsion had contributed significantly to make polymer distribution in wood uniform. Incorporation of strong hydrophilic character of wood is regarded to be the principal reason for such a favorable result.

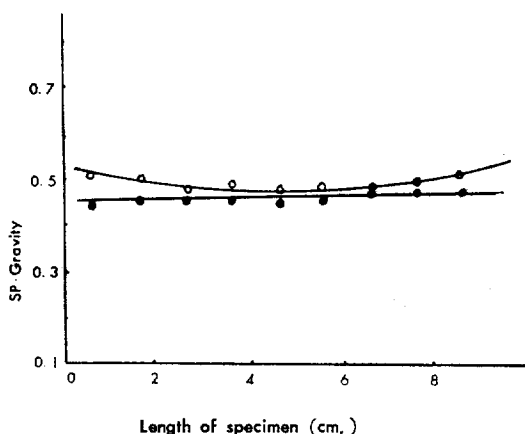


Fig. 1. Sp. Gravity distribution of polymerized specimens.

○ ; Bulk polymerized, Polymer content is 27.3%

● ; Emulsion polymerized, Polymer content is 16.7%
 ✕ Sp. Gravity of original wood is 0.432.

The result showing low value of specific gravity at the central part of specimen which obtained from pure styrene polymerization is quite consistent with the result discussed in our previous work⁸⁾, which treated the longitudinal distribution behavior of Lauan with styrene monomer. According to the previous observation, the loaded quantity at position about 5 cm. away from the monomer diffusing surface was reduced to about 63%. Such reducing tendency of pure monomer in quantity at the central part of specimen might be partly due to the fact that the wood has forced the hydrophobic monomer to fill only in the voids of wood without allowing any additional permeation or diffusion through the transient capillaries of the cell wall. Also the air presented in the capillaries of the central part of the specimen might hinder the fluid flow through capillaries.

Siau et al⁹⁾ already observed somewhat concave-downward variation of specific gravity of yellow birch-polymethyl methacrylate combination in their study of properties of heat and radiation cured wood-plastic composites. An interpretation was that the evaporation of monomers during polymerization caused the decrease in specific gravity at the end parts of the specimen. This means that, if the loss of monomer due to evaporation could be prevented by better wrapping of specimen, there is no reason for the specific gravity to be reduced at the end parts of specimen. Rather, it is believed that there is greater possibility of increase in the concentration of polymer at the outer surface or end parts of the specimen by squeezing the monomers outward during the polymerization, owing to the shrinkage of wood on heating.

In Fig. 2 have been illustrated the overall volume changes of specimen due to water absorption. The dimensional stabilities of both products from emulsion and bulk polymerization in water have increased with the increments of polymer content, as shown in Fig. 2. The specimen containing 43% of polymer revealed only 8% of volume expansion, but the specimen non-polymerized expanded to about 12%.

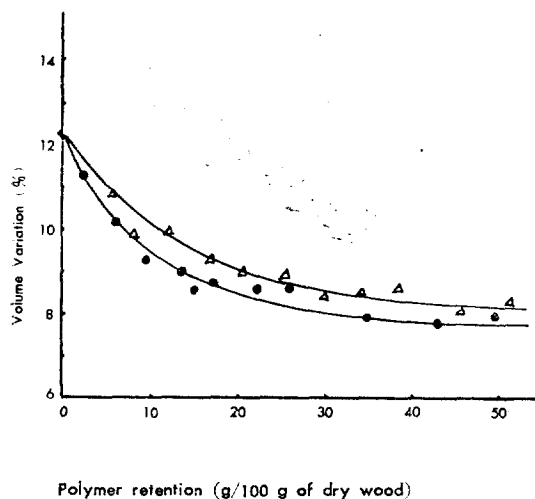


Fig. 2. Polymer retention vs. volume variation in water

△ ; Pure styrene
● ; Emulsified styrene

In comparison of their effects extending to the dimensional stability, the product from emulsion turns out to be more effective. An appropriate directive influence to provide uniform dispersion of polymers by allowing extraneous diffusion of monomers through the transient capillaries is presumed to be occurred when the emulsion is involved.

The longitudinal diffusion of water with varying contents of polymer by emulsion polymerization serves well to give an improved hydrophobic behavior of wood treated with emulsion, as illustrated in Fig. 3. The remarkable reduction of diffusion rate even at low concentration of polymers in wood gives the evidence of uniform dispersion of polymers. The fact that the longitudinal diffusivity of emulsified specimens containing polymers 10 to 50% are reduced with the rates ranging 70.2 to 78.7% provides the evidence of the effectiveness in prevention of the absorption of water induced by diffusion mechanism. Also, as Fig. 3 revealed, the trend of showing no great difference in diffusivities between specimens retaining polymers from 10 to 50% leads to a conclusion that the diffusion of water through the longitudinal direction of emulsion

polymerized specimen can be stopped effectively by distributing a small quantity of polymer uniformly.

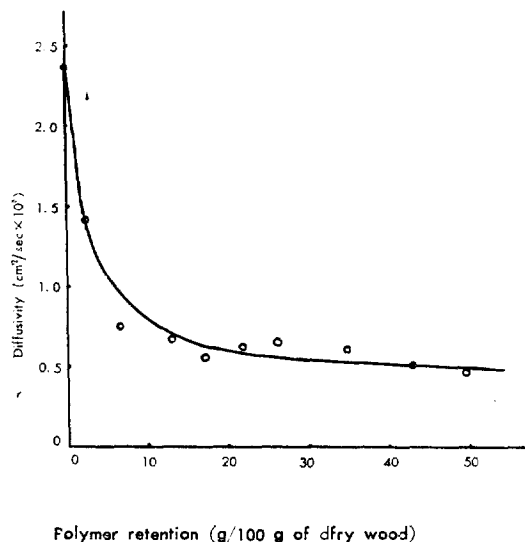


Fig. 3. Polymer retention vs. longitudinal diffusivity of water

○ ; Emulsified styrene

It is of interest also to note that the value of diffusion coefficient of water determined from the specimen containing 50% of polymer is $4.38 \times 10^{-7} \text{ cm}^2/\text{sec}$, and this agrees very closely with the value of $4.95 \times 10^{-7} \text{ cm}^2/\text{sec}$ obtained by Siau⁹ from a specimen of methyl methacrylate-polymerized yellow birch sap wood.

In order to observe the response of reinforced product to the lateral force, lateral compressive strengths with both emulsion and bulk polymerized specimens were measured. As clearly indicated in Fig. 4, the emulsified products exhibited a linear increase of strengths with the increments of polymer loading. The relationship between the compressive strength and polymer retention in bulk polymerized specimens was similar to that of emulsified specimens within the range of 10% of polymer content, but when the polymer content exceeded 20%, emulsified specimen revealed higher value of compressive strength. As the distinctive reduction of longitudinal diffusivity of emulsified specimen was due to the uniform dispersion of polymer along to that direction, homogeneous dispersion of polymers from emulsion to the longitudinal direction appeared to have contributed to yield the greater

increase in strength than in the case of the bulk polymerized.

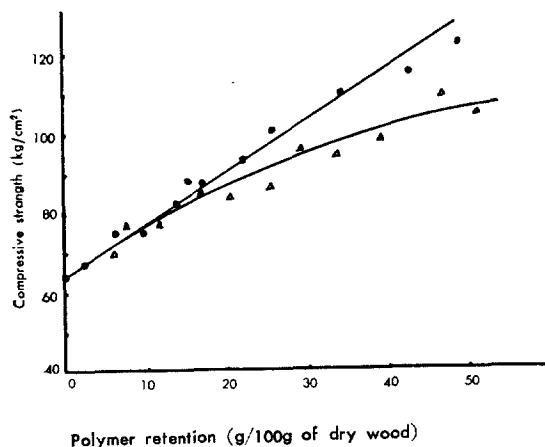


Fig. 4. Polymer retention vs. lateral compressive strength.
 \triangle ; Pure styrene
 \bullet ; Emulsified styrene.

The fact that the strengths of both products have shown somewhat identical at relatively low range of polymer concentration would be due to the minor effect of polymers in extending their strengths toward the original strength of wood.

Tests of Brinell hardness to the surfaces of radial direction were conducted. The bulk polymerized specimen showed great irregularities of hardness. Such a result might have arisen from the localization of polymers at the outer layers of specimen. On the other hand, the hardness of emulsified specimens increased with the polymer contents as shown in Fig. 5. But it is interesting that the improvement of hardness is not proportional to the amounts of loaded polymer except when the polymer contents are low. The nature of this behavior is considered to be brought about by the limitation of existing hardness of pure polystyrene.

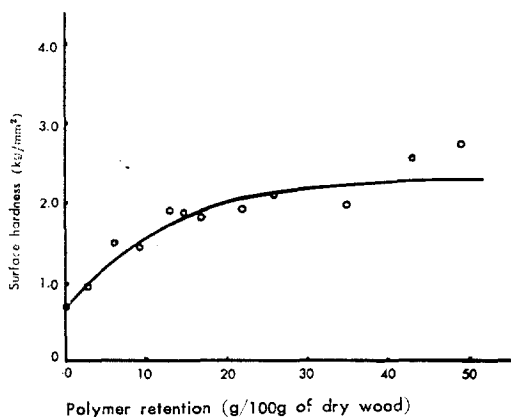


Fig. 5. Polymer retention vs. surface hardness of emulsified products

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