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목재에 대한 Vinyl 계 단량체들의 침투 및 분포 거동에 관하여

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Impregnation and Distribution Behavior of Vinyl Monomers to Wood

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요 약

활엽 및 침엽樹種에 對한 Vinyl 系 單量體들의 침투 및 分布거동에 關하여 考察하였다. 特히 木材內에서 單量體 分布의 均一性 여부와 Diffusion 에 依한 單量體의 流動 현상에 關하여 관찰하였다. Diffusivity 는 Void volume의 크기에 比例하였으나 均一性 여부는 木材의 Fluid pathway 구조에 依한 영향이 컸다. 활엽수종은 MMA 를, 침엽수종은 styrene 을 各各 더 많이 침투시켰다.

Abstract

Overall impregnation behaviors with vinyl monomers to some leaf and needle woods and their distribution in woods are described. Attention is directed toward the observations of both the monomer uniformity in wood and fluid flow by diffusion mechanism which is one of the important processes in practical impregnation treatments of bulk wood. Diffusivity is appeared to depend on the percentage of void, but the uniformity of fluids in wood is found to be primarily limited by the nature of fluid pathways. Leaf woods show their affinities to MMA, but pines have exhibited their preferences to styrene.

Introduction

Many papers[1~5] reported some of promising results on the preparations of more effective wood-plastic combination (WPC), but most of them were focussed on the evaluation of mechanical behavior of reinforced product or on the establishment of economical impregnating processes.

A few systematic investigation[6~8] on the penetrability of organic fluids to woods had been reported. But it is still known that the homogeneous distribution of hydrophobic organic liquids in wood is difficult owing to both the complicated structure of the capillary system and the versatility in nature of wood compositions.

In order to establish proper conditions for making more effectiv WPC with some leaf and needle woods, the behaviors of impregnation and distribution of hydrophobic vinyl monomers in woods have been observed. Since impregnation of wood with liquid involves penetration and flow through capillaries, emphases are placed particularly upon the measurements of effective diffusivity and the observation of uniformities of monomers in wood.

Experimental

1) Materials

Woods; The species investigated were the sap woods of Lauan, Populus euramericana, Pinus densiflora, and Pinus rigida. Specimens were prepared by cutting into definite sizes along the longitudinal direction, and controlled to have constant moisture content at room temperature by steaming and drying under reduced and atmospheric pressure.

Monomers; Vacuoum distilled styrene and MMA were used as the impregnating liquids.

2) Measurements and Calculations

Physical properties of conditioned specimens; The apparent specific gravity (Sp. Gr) and the Sp. Gr. in oven dry were measured according to the JIS Z 2102. Moisture content and void volume percentage of wood were calculated by the following equations[9];

$$U=\frac{G_u-G_o}{G_o}\times 100$$

$$C=(1.00-\frac{r_o}{1.50})\times 100$$

where U; moisture content of specimen

G_u; weight of original specimen

G_o; weight of specimen that equilibrated at 100—105°C

C; percentage of void volume

r_o; Sp. Gr. in oven dry

Monomer content and its uniformity; The loaded quantity of monomer against the time of immersion and its uniformity in wood were determined as follows. Specimen for loading test was cut into a shape of slab sized as 2×2×1 cm, and sealed perfectly all the thin edged surfaces with epoxy resin so that diffusion could take place only toward and from the flat parallel faces. After perfect drying, weighing of specimens, they were immersed into a monomer bath at constant temperature. Each immersion was carefully controlled to occure the diffusion to vertical direction. And the depth of immersion was fixed to prevent pressure differences in specimen during the processing. Such immersion of specimen into monomer bath was continued until the weight of specimen became constant.

The specimen for the evaluation of monomer uniformity in wood toward longitudinal direction was prepared to have its dimension 0.5×0.5×1.0 cm (rectangular bar shaped), and also sealed all the faces with epoxy resin except one face at the longitudinal bar end through which diffusicn can take place. Specimen conditioned was fixed vertically to maintain constant depth of immersion and upward direction of diffusion. Then monomer was flushed in to give the specimen soaked completly. After immersion of specimen in monomer bath for about 50 hours under atmospheric pressure, specimen was weighed and cut into several pieces of blocks with identical dimension. Then the weight of each block was measured.

Effective diffusivity; With assumptions that there would be no bulk flow and no chemical reaction during immersion, unsteady state diffusion from a slab with sealed edges, one of the Newman's modifications[11] of Fick's second law, was applied. The effectiv diffusivity, D, was then calculated with following equation[11] by deriving experimentally the fraction loaded, E, at time θ, and by computing function f from a known graph.[10]

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

where E; the fraction loaded

C_{Ao}; initial monomer concentration in wood

$C_{A\theta}$; monomer concentration in wood at time θ

$C_{A\infty}$; saturated monomer concentration in wood

D; effective diffusivity

a; diffusion length of specimen

Results and Discussion

Specific gravity; An apparent Sp. Gr. of wood is an important property for both the estmations of the mechanical strength of wood and of the amounts of liquid to be impregnated because it pertains directly to the percentage of void vloume of wood. **Table 1** shows the physical properties of controlled original

Table 1. Physical properites of controlled wood specimens.

Properties	Woods: Lauan	Populus	Pinus rigida	Pinus densiflora
Sp. Gravity	0.481	0.299	0.503	0.404
Sp. Gravity in oven dry	0.461	0.293	0.494	0.394
Void volume(%)	69.3	80.5	67.1	73.7
Moisture content(%)	4.35	1.87	2.01	2.72

wood specimens. The severe discrepancy in Sp. Gr. between Lauan and Populus, even they are same leaf species, proves the large difference of cellular structure. The occurence of variety in cell forms like Tracheid, Vessel, Libriform wood fiber, Wood parenchyma, Ray, and Intercellular spaces[12] in leaf woods is belived to give the possibility of irregular appearance in physical properties.

The Pines, however, showed relatively small variations in their Sp. Grs. An anatomical Observation proved that the Gymnosperms[13] were fairly homogeneous because they were consisted basically of only two cell types, the longitudinal Tracheid and Ray cells.

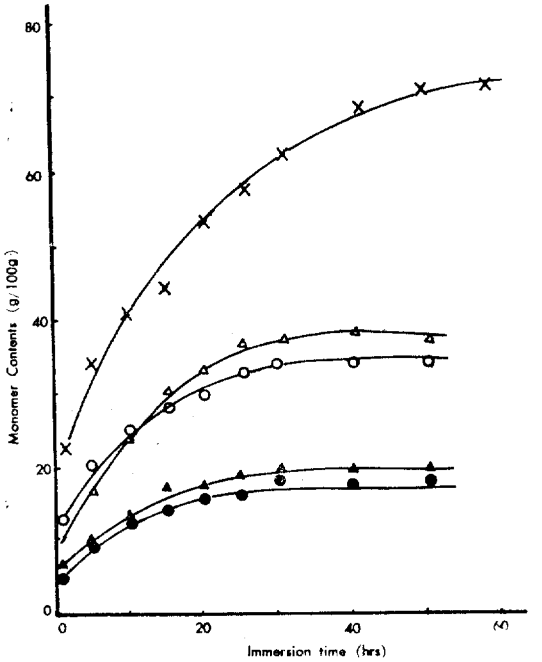

Fig. 1, Monomer content variations of Lauan against immersion time
×; water (longitudinal)
○ : styrene(//)
△; MMA (//)
●; styrene (lateral)
▲; MMA (//)

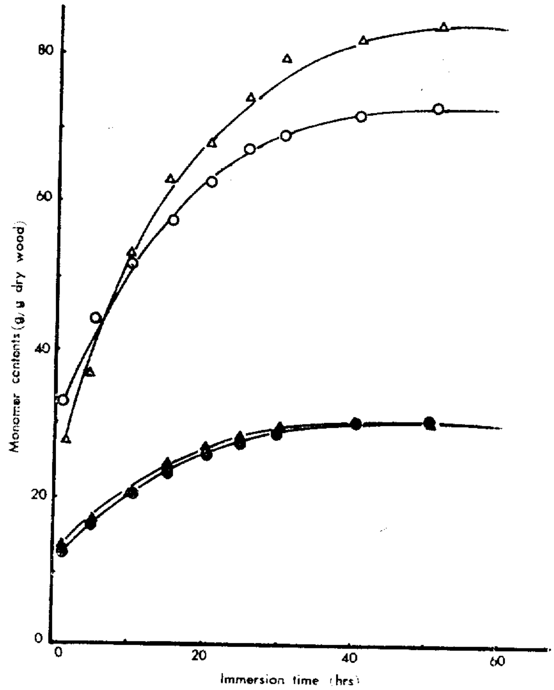

Fig. 2, Monomer content variations of Populs against immersion time
○ : styrene (longitudinal)
△ ; MMA (//)
● ; styrene (lateral)
▲ ; MMA (//)

On the basis of such structural simplicity, Pines can be assumed as the species which is rather promising for that a fairly uniform distributin of monomer in wood can be attainable.

Overall impregnation behavior; Although wood has been known as a porous material, variabilities in physiological processes and complexities of fluid pathways have caused difficulties to establish an unique model of impregnation behavior of liquids to wood. In order not for encountering differences arising from the process of impregnation, external conditions were settled as to maintain constant temperature and the depth of immersion.

As indicated in **Fig. 1**, a distinguished behavior of impregnation of water to Lauan was observed. This would be resulted from the fact that the extraordinary hydrophilic character of woods has probably forced water to proceed additional diffusion through the capillaries of the cell walls of wood.

The impregnation behavior of hydrophobic vinyl monomers, as clearly indicated in Fig. 1 to 4, was primarily controlled by the size of voids presented in wood, no matter what the species of woods or complexities of fluid pathways. And it was cleared also that the total quantity of diffused monomer was depended largely upon the amounts of longitudinal diffusion. The accurate interpretation of these results, it is believed, may require an correct appreciation of the anatomical functions of each cell or cell structure of woods.

It is of interest also to note that MMA showed a little higher value of loading than styrene in leaf woods, whereas styrene diffused more quantity than MMA to needles, as appeared in Fig. 1 to 4. Relative viscosities of styrene and MMA at 24°C were 0.86 and 0.64, respectively. If the affinity of both monomers toward a speciffc wood is in the same order under definite impregnation condition, liquid with low viscosity and smaller molecular size would move more readily into the narrower spaces.

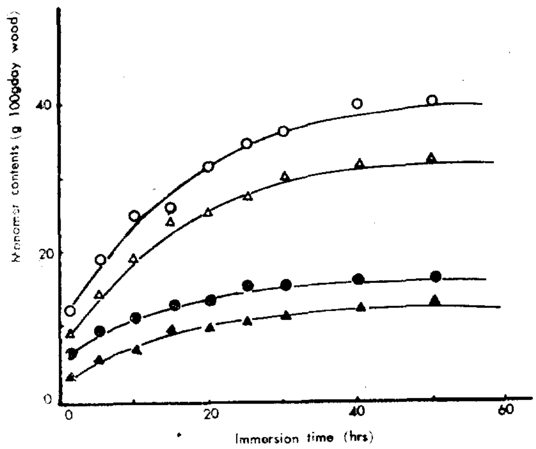

Fig. 3. Monomer content variatons of Pinus rigida against immersion time
○ ; styrene (longitudinal)
△ ; MMA (〃)
● ; styrene (lateral)
▲ ; MMA (〃)

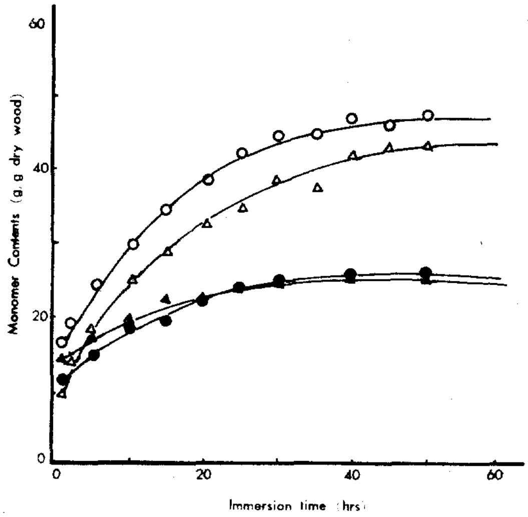

Fig. 4, Monomer content variations of Pinus densiflora against immersion time
○ ; styrene (longitudinal)
△ ; MMA (〃)
● ; styrene (lateral)
▲ ; MMA (〃)

Although the Kitahara's findings[14] that there have been appered 200 to 400 of cell pits sized 10^{-3} cm in diameter per cm^2 of cross sectional area of Pines implies the possibility to provide substantial pathways for bulky or viscous fluids through these larger pits, the reason that the styrene has shown more affinity to needle, as indicated in Fig. 3 & 4, is hardly interpretable terms of only viscosities or molecular size of impreg nating fluids. The presence of resins and resin canals in both the lingitudinal and radial direction in Pines might be affected on the higher amounts of loading of aromatic hydrocarbon, styrene. Resin canals in the sapwood of Pines are known to give particular effectiveness on permeability of fluid[13] and the resins contained in canal can be readily changed into volatile terpene and nonvolatile Colophonium by simple exposure of resin to steam. Since these compounds were mainly consisted with hydrocarbon, they might give rise of affinity and miscibility with styrene so that additional amount of styrene could be loaded.

Diffusivity; Since the diffusion is one of the most important mechanisms of fluid penetration to wood, determination of diffusivity may provide a means of visualizing the essential behavior of impregnation of monomer to wood.

It was well recognized that diffusion in solid with irregular structure such as wood was distinguished as structure sensitive diffusion.[11] However, in the present work, the determination of diffusivity was attempted under the assumptions that the nature and size of voids were uniform in all direction and in every part of the specimen. The diffusivity in solid may vary very rapidly with temperature and the flow pressure may arise due to the pressure differences in the operating system, thus the external conditions such as temperature and pressure are maintained constantly.

As indicated in Table 2, the distinct difference between water and monomer in diffusivity for the same wood(Lauan) demonstrates clearely the dependence of hydrophilic character of penetrant on the degree of diffusion. Therefore, attaining high diffusivity of hydrophobic organic liquids under normal pressure is considered to be impossible except when the impregnant is properly modified to retain hydrophilic character.

Table 2. Effective diffusivities of monomers to various woods.

Woods	Monomers	Diffusivity($cm^2/sec \times 10^6$) Longitudinal	Lateral
Lauan	water	2.380	
	styrene	1.503	1.049
	MMA	1.549	1.099
Populus	styrene	2.633	1.432
euramericana	MMA	2.704	1.454
Pinus rigida	styrene	1.561	0.871
	MMA	1.515	0.794
Pinus	styrene	1.687	1.106
densiflora	MMA	1.564	1.180

In comparison of diffusivities between longitudinal and lateral direction, as shown in Table 2, Populus revealed the highest value of difference among the specimens. Absence of detectable openings in lateral direction, as usually obseved in some leaf woods, and the existence of the annual ring was believed to keep

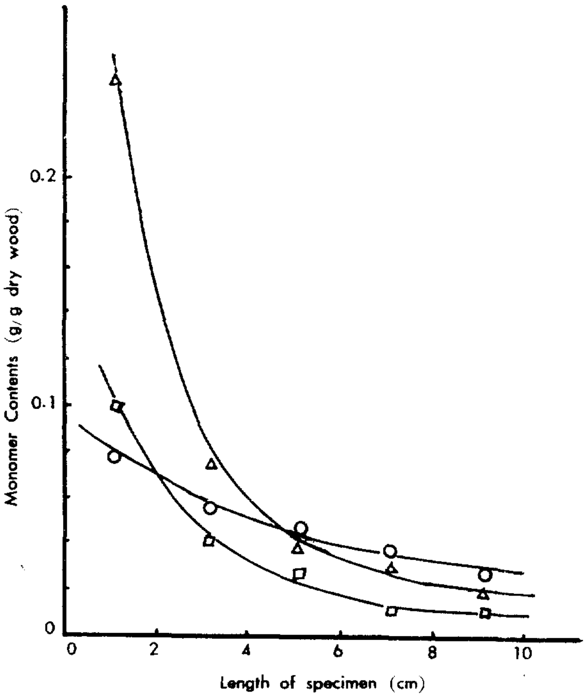

Fig. 5, Longitudinal monomer (styrene) distribution in wood
○ ; Lauan
△ ; Populus euramericana
□ ; Pinus densiflora

the lateral amount of diffusion from increasing. In contrast to Populus, Lauan, a leaf wood, showed the most prominent in reducing the difference of diffusivity between the longitudinal and lateral direction. It was considered that this result was attributable to the facts that Lauan, growing at tropical zone, had nothing detectable annual ring, and hence it should be a such structure of diffusion porous.

The feature, on the other hand, that the two Pines have shown a fairly similar behavior in diffusivity is presumably due to their structural simplicity. From the results obtained, it could be concluded that the overall diffusivity of hydrophobic monomers to woods is able to be predicted by observing the void volume and void structure of woods.

Monomer uniformity; As demonstrated by Mittienen,[15] a more effective WPC is not just a wood containing merely large amounts of polymer, but a wood with homogeneously distributed polymer. Thus the influence of anatomical structure of wood appeares to be one of the major factors affecting a homogeneous distribution of fluids in it.

Fig. 5 shows the dependence of styrene distribution on the length of wood specimen. Although Populus yielded the greatest diffusivity at longitudinal direction, the concentration of monomer was higher at the vicinity of diffusing surface of specimen. This may be resulted from the fact that the vessls are usually blocked with tyloses[16] and the arrangement of vessel is highly intervened with annual ring, since leaf wood like Populus is ring porous rather than diffusion porous, thus the fluid flow through the capillaries or interstices is disturbed significantly.

The content variations of Pines along the longitudinal direction seems to be influenced by the blocking of longitudinal Tracheid in a similar manner shown by Populus. Following the Elwood's indication stating the end closure of longitudinal Treheid of Gymnosperms,[17] the feature exhibiting unevenness in distribution should obviously be remained about the same as for the case of Populus.

On the other hand, the tendency of Lauan toward monomer uniformity is the most promising and outstanding. A leaf wood like Lauan growing at the tropical area has not only regular arrangement of vessels by elimination of interference caused by annual ring formation, but has well vertically developed intercellular spaces.[18] This initial regularity in longitudinal arrangement may naturally extended to force the formation of diffusion porous system. The so caled "diffusion porous wood" is also known as a wood retaining absolutely little tyloses.[16] Both the beneffcial situations, lacking of tyloses in vessels and sufficient vertical intercellular spaces, should be in favor to facilitate the continuous vertical fluid flow.

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