

《Original》 A Study on the Preparation of Wood-Plastic
Combinations(Ⅲ) Preparation of Wood-Plastic
Combinations by Thermal Curing Method

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Abstract

The polymerization rates of monomer or monomer mixture impregnated with catalyst into domestic soft woods such as *pinus densiflora*, *pinus rigida* and *populus deltoides* *e.t.c.* were measured. The results were compared with those obtained by radiation curing method and the following conclusions were derived;

(1) *Pinus densiflora* and *pinus rigida* are superior to the *populus deltoides*, and methyl methacrylate(M.M.A.) is more effective than other monomers as far as the polymerization rates are only taken into account.

(2) The polymerization rate of vinyl acetate is generally slow. And the polymerization rate of the monomer is the slowest in case of being impregnated into *populus deltoides*. However, the polymerization rate of the comonomer composed of vinylacetate and M.M.A. is the fastest among the other monomers or monomer mixtures in woods regardless of the curing method.

(3) The general trend of polymerization of monomer in wood is similar to that of monomers themselves in both curing methods if the woods contain not much resin.

요 약

육송 미송 포플라등 국산 연질 목재에 단량체 또는 단량체 혼합물을 촉매와 함께 침투시키고 열중합함에 있어서 시간에 따르는 중합율을 구하고 이것을 방사선 중합으로 WPC를 제조할때 얻은 값과 비교 검토하여 다음과 같은 결론을 얻었다.

(1) 중합율로 보아서는 육송, 미송이 포플라보다 좋으며 M.M.A.가 다른 단량체보다 효과적이다.

(2) 비닐아세테이트는 일반적으로 열중합에 의한 중합율이 저조한 편이며 특히 포플라에 침투된 경우 매우 낮아 W.P.C.를 만들기 곤란하다. 그러나 비닐아세테이트와 M.M.A.를 같이 침투시키면 나무종류나 중합방법에 별 관계없이 매우 빨리 중합하여 가장 효과적이다.

(3) 나무에 침투된 단량체나 단량체 혼합물의 중합의 경향은 나무가 많은양의 수지를 함유하지 않는다면 중합방법에 관계없이 단량체나 단량체 혼합물 자체만일때의 중합의 경향과 같다.

1. Introduction

It is well known that the radiation curing method has further advantages such as the adaptabilities of consecutive operation in large scale, and the easiness in control of polymerization rates comparing with thermal curing method in the preparation of W.P.C.^{1, 2)}

However, in small scale production, the thermal or chemical curing method would be profitable because of its lower cost investment for the facility and easier workability without any radiation hazard.

It has been reported that the preparation of W.P.C. by thermal curing method using yellow birch³⁾ and Hornbeam⁴⁾ *e. t. c.* as wood material. The monomers used were M.M.A.³⁾, and styrene-acrylonitrile mixture and polyester⁴⁾. It is so described in the literature that the properties of W.P.C. products obtained by thermal curing method are not much different from those of W.P.C. obtained by radiation curing. However, any detailed data on the polymerization rate are hardly found.

In this paper the authors have investigated on the polymerization rate and polymerization conditions in the preparation of W.P.C. by thermal curing method using domestic soft woods and conventional monomers. As a succeeding study on the preparation of W.P.C. by radiation curing method the data obtained in the W.P.C. preparation by thermal curing are compared with those obtained in radiation curing.

2. Experimental

(1) Impregnation of Monomers and Comonomers

The monomer containing 0.2% of benzoyl peroxide is impregnated in wood according to the method previously reported⁵⁾. The monomers of styrene, M.M.A. and V.A. *e. t. c.* were used. To get higher accuracy in the

measurement of polymerization rates 15 to 20 samples were prepared with the same kind of wood and the same kind of monomer. In the impregnations of comonomers, the monomer containing 0.2% of benzoyl peroxide was mixed in 1:1 volume ratio with another monomer in which contains also the same amounts of the same initiator. Such a comonomer was impregnated in the way just like the single monomer. To protect the monomer evaporation during curing the surfaces of the sample pieces were coated with polyvinyl alcohol(P. V. A.) film according to the previously reported procedure⁵⁾.

(2) Thermal Curing

The sample pieces were placed in an oven of which temperature was controlled to $70 \pm 0.5^\circ\text{C}$. After definite time intervals, some samples were taken out to measure the polymerization rates. The samples were washed to remove P. V. A. film and fully evacuated in vacuum desiccator until they show constant weight. By the way the unpolymerized monomer or even oligomer in wood could be removed. From the differences in weight the polymerization % could be determined(Fig. 1-4).

3. Results and Discussion

(1) Preparation of W. P. C. using Single Monomer

M.M.A. in populus deltoides is rapidly polymerized to give 80% polymerization in 3 hrs. at 70°C . In contrast, V.A. is very slowly polymerized in the same wood to give only 4% polymerization under the same conditions (Fig. 1). Styrene is moderate in polymerization rate to give 25% polymerization. However, when styrene or V.A. is impregnated in pinus densiflora or pinus rigida the polymerization rates are increased a little although these woods contain more resin comparing populus deltoides. It signifies that the resin in

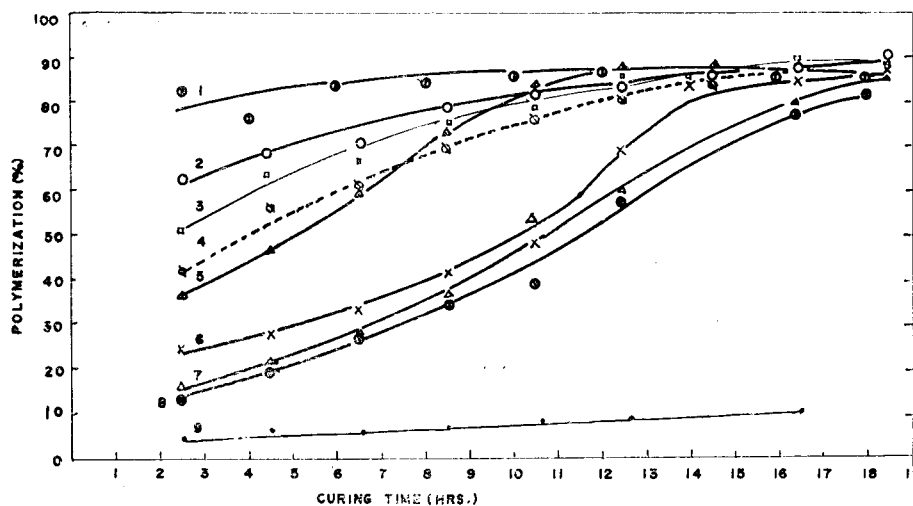


Fig. 1. Polymerization % of the impregnated monomers as a function of curing time

- | | |
|--------------------------------|-------------------------------|
| 1. populus deltoides-M. M. A., | 2. pinus rigida-styrene, |
| 3. pinus densiflora-styrene, | 4. pinus rigida-M. M. A., |
| 5. pinus densiflora-M. M. A., | 6. populus deltoides-styrene, |
| 7. pinus densiflora-V. A., | 8. pinus rigida-V. A., |
| 9. populus deltoides-V. A. | |

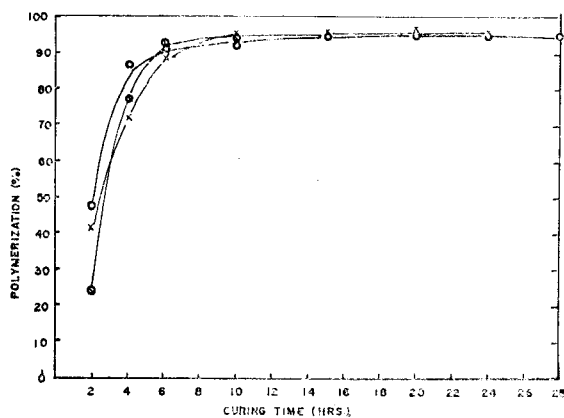


Fig. 2. Polymerization rates of comonomer (M. M. A. + V. A.) in woods

- x-: pinus densiflora, -o-: pinus rigida,
-⊖-: populus deltoides

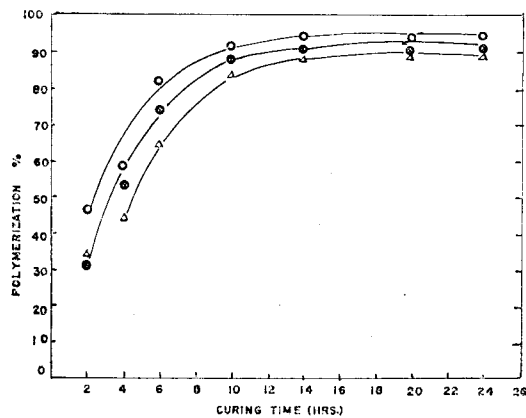


Fig. 3. Polymerization rates of comonomer (M. M. A. + styrene) in woods

- ⊗-: pinus densiflora, -o-: pinus rigida,
-Δ-: populus deltoides

populus deltoides consisted with much more components which acts as an inhibitor in the polymerization of styrene or V. A.

In the radiation induced polymerization V. A. in pinus densiflora is the fastest in polymerization rate to bring about 100% polymerization under the dose rate of 4×10^4 rad/hr. and the total dose of 4 Mrad⁵⁾.

Consequently, the polymerization rate of

V. A. is fast in radiation curing but it is quite slow in thermal curing. The cause of the great difference in rate is still not clear in so far as the reactions are accomplished via free radical propagation mechanism in both curing methods. In radiation curing, the polymerization rate of styrene monomer in wood is slow in initial stage but it is slowly increased with total dose. However, in thermal curing, the

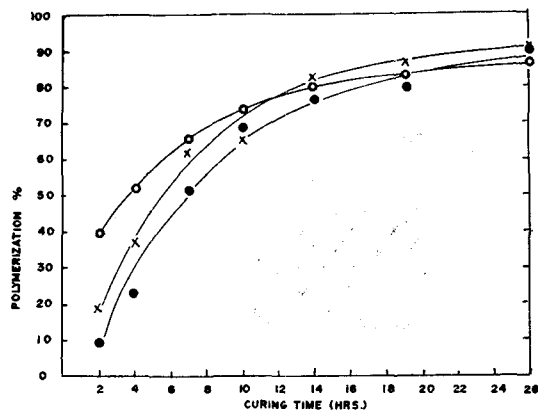


Fig. 4. Polymerization rates of comonomer (V.A +styrene) in woods
 -x-: pinus densiflora, -o-: pinus rigida,
 -●-: populus deltoides

rate is 5 to 6 times faster than that of vinyl acetate even in initial stage (Fig. 1). M. M. A. is the most promising since it is the fastest in polymerization rate among the monomers in both curing methods.

(2) Preparation of W, P, C, using Comonomers

The polymerization rates of comonomers in wood are dependent only upon the components of the comonomer and almost independent upon the wood material. The polymerization rates of comonomers in pinus rigida are slightly faster than those of the comonomers in populus deltoides (Fig. 2, 3, 4). When M. M. A. is a component of the comonomer system the polymerization rates are always fast. As Fig. 2 shows, the comonomer composed of M. M. A. and V. A. is polymerized perfectly in 8 hrs. at 70°C. It is also observed that the polymerization rate of the comonomer in pinus densiflora is slightly faster than that in other woods but the difference is not much comparing that in the W. P. C. preparation using single monomer. As shown in Fig. 3, the polymerization rate of the comonomer consisted of M. M. A. and styrene is a little bit slower than those of M. M. A. + V. A. comonomer under the same conditions. The slowest is the comonomer

consisted of V. A. and styrene.

Considering that the polymerization rate of M. M. A. is the fastest and that of V. A. is the slowest in single monomer, it is expected that the polymerization rates of M. M. A. comonomers with styrene or with V. A. are faster than those of respective single monomer; *i.e.*, styrene or V. A. Consequently, the order of polymerization rate will be $M. M. A. > M. M. A. + \text{styrene (comonomer)} > M. M. A. + V. A. \text{ (comonomer)}$, as far as there is not any interaction between two monomers in wood. However, the copolymerization between M. M. A. and V. A. seems to occur considering the fact that the rate of V. A. is slower than that of styrene when impregnated as a single monomer in wood but the rate of comonomer composed of M. M. A. plus V. A. is faster than that of comonomer composed of M. M. A. plus styrene.

According to the data reported by Mayo and Walling⁶⁾ the polymerizabilities of M. M. A. monomer to styrene radical and to V. A. radical are 1.3 and >5 , respectively. Thereupon, it may be said that the rate of copolymerization between M. M. A. and V. A. is faster than that between M. M. A. and styrene. Further, it may be said that the general trend of rates of polymerization and copolymerization are not varied even when the monomer or monomers are impregnated in wood of poor resin contents. The order of polymerization rate, $M. M. A. + V. A. > M. M. A. + \text{styrene} > V. A. + \text{styrene}$ coincides well with that obtained in the radiation curing method. As far as the polymerization rate is only taken into account, M. M. A. is the most suitable monomer and M. M. A. + V. A. is the most suitable comonomer. M. M. A. + V. A. in wood shows 100% polymerization in 10 hrs. at 70°C., and shows 80% polymerization in 5 Mrad of total dose of which rate is 4×10^4

rad/hr.

4. Conclusions

The conclusions derived through this study are as follows;

(1) Polymerization rate of V. A. impregnated in populus deltoides is so slow that it is not suitable for W. P. C. preparation by thermal curing method.

(2) The polymerization rate of M. M. A. in wood is quite fast regardless of the wood materials.

(3) The polymerization rate order of M. M. A. + V. A. > M. M. A. + styrene > V. A. + styrene is just coincide with that observed in radiation curing.

(4) As far as the polymerization rate is only taken into account, pinus densiflora and pinus rigida are more suitable wood materials than populus deltoides, and M. M. A. is more effective than other monomers. The comono-

mer composed of M. M. A. plus V. A. is the most promising.

(5) The general trends in polymerization rates of monomers or comonomers in wood are similar to those in polymerization rates of monomers or comonomers in bulk, as far as the wood contains not much resin.

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