

◀Original▶ **Preparation of Slate-Plastic Composite**

Hyung Chick Pyun, Bong Rae Cho and Suk Keun Kwon

Korea Atomic Energy Research Institute, Seoul, Korea

(Received July 30, 1974)

Abstract

Slate-plastic composite was prepared by impregnating methyl methacrylate monomer into the slate and subsequent curing the monomer either by gamma radiation or by thermal-catalytic method.

Experiments were carried out to determine the polymerization rate and to investigate the properties of the composite. Significant improvements in flexural strength, water absorbability and acid resistance were observed in the products. Differences in properties between the composites obtained via two different methods were discussed as well as the cause of such results.

요 약

슬레이트에 단량체 methyl methacrylate 를 침투시키고 감마선 및 촉매 가열법으로 중합시켜 슬레이트-플라스틱 복합체를 제조하였다. 제품의 성질은 휨강도, 내수성 내산성등에 현저한 증가를 나타내었으며, 중합조건에 의한 차이점도 그 원인과 함께 비교 검토하였다.

1. Introduction

The research on concrete plastic composites grew out of wood-polymer combination, where radiation or catalyst was used to polymerize the monomer impregnated in the wood. As it was observed that wood-polymer combinations have improved strength and durability properties, attempts were made to make the concrete analogue of wood polymer¹⁾. The results were so encouraging that the studies on the application of concrete-plastic composite (CPC) to various fields such as desalination plants, highways, bridges, breakaway posts,

pipings and railroads etc. have been extensively carried out^{2,3)}.

The authors also have investigated on the process of preparation and the properties of the mortar-plastic composite⁴⁾. In this work, we have choosed slate and methyl methacrylate as the raw materials of the composite and the investigation was focused on the curing methods and the differences in the properties of the products.

2. Experimental

1) Materials and Instruments

a) Slate specimens; Asbestos slate(thick-

ness: 5.5mm, density: 1.8g/cm³) from H. Co. was cut to 50×150mm.

b) Monomer: Technical grade methyl methacrylate (MMA) was washed with alkali solution and distilled under reduced pressure.

c) Radiation source and Tester: Co-60 γ -irradiation facilities of 25,000 Ci and testing machine of "Shimadzu Autograph TYPE TS-5,000".

2) Preparation of Slate-Plastic Composite (SPC)

a) Impregnation of monomer

Slate specimens were dried in a drying oven maintained at 120°C and evacuated to 1-2 mmHg in a small vacuum desiccator for 30 minutes and soaked in MMA monomer. MMA-impregnated slate was wrapped in Al-foil (thickness: 0.025mm) to reduce the evaporation loss of monomer during its polymerization period.

b) Polymerization

(1) Thermal-catalytic polymerization

The slate was impregnated with MMA containing 2.0% benzoyl peroxide (BPO) and polymerized in the drying oven maintained at 80°C.

(2) Radiation polymerization

MMA-impregnated slate was irradiated under the radiation intensity of 0.7 Mrad/hr varying the total dose.

3) Measurement of properties of SPC

a) Water absorption

Dried specimens were immersed in distilled water at 20°C, removed and reweighed periodically. The increased weight % of immersed specimens was taken as the water absorption.

b) Acid resistance

Dried specimens were immersed in 15% HCl

solution for 48 hrs, washed with water, dried and reweighed. The weight loss was determined as the corrosion resistance to the acid.

c) Flexural strength

The flexural strength of the specimen was determined by using the testing machine. Constant weight of 100kg, with the cross head speed of 0.25mm/min, was applied on the center of the specimen with 10cm span. The applied load at the instant of breakage was read, and transformed into the flexural strength using the following equation⁵⁾.

$$\text{Flexural strength} = M/Z (\text{kg/cm}^2)$$

$$M = Pl/4, \quad Z = bd^2/6$$

where, P : load(kg),

l : span(cm),

b : width of specimen(cm),

d : thickness of specimen(cm),

3. Results and Discussion

1) Preparation of SPC

The amount of monomer that can be loaded in a slate specimen is limited by the amount of free water and air occupying the total void volume. To achieve maximum monomer loading, slate specimens should be completely dried and evacuated prior to be impregnated.

According to Fig. 1, it is clear that the water content of the slate is about 5 wt. %, and more than 3 hrs is required to dry it completely under the condition. Fig. 2 shows the rate of MMA impregnation through slate. Monomer loading was determined by weight increase. Complete impregnation of monomer occurs within 10 minutes and at this point the monomer loading is 17 wt. % under reduced pressure. But on atmospheric condition, 12 wt. % of MMA is impregnated. This result is nearly 2 or 4 times more than the wt. %

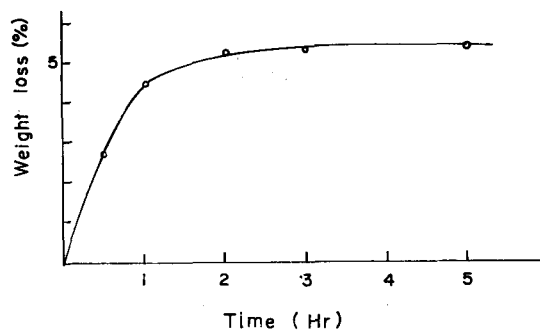


Fig. 1. Drying curve for slate at 120°C

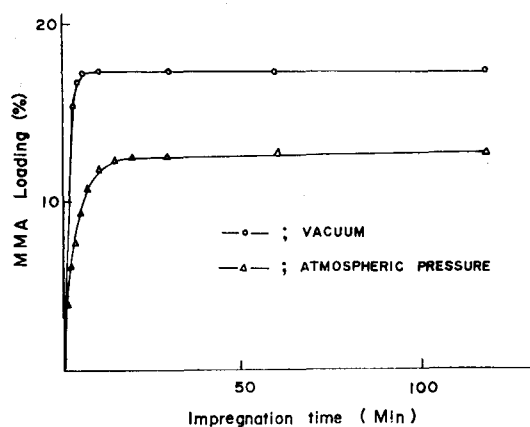


Fig. 2. Impregnation % vs. impregnation time for MMA monomer at 32°C.

of impregnated monomer in mortar⁴⁾ or concrete^{1,6)}. Compared with the data^{1,4,6)} of water content and monomer loading obtained for slate, mortar and concrete, we conclude that slate is more porous than mortar or concrete and can be impregnated with monomer more easily.

Table 1 shows the evaporation loss of monomer from the impregnated slate specimen during the polymerization. The loss depended on the polymerization temperature and the time required for polymerization as expected. But the maximum loss was only 2.6% of the total MMA impregnated.

The polymerization of the impregnated monomer has been carried out without any

serious difficulties in either curing method of radiation or of thermal-catalyst. But the appearances of the product were quite different depending on the curing methods. In the product cured by radiation, the distribution of the polymer loaded was almost uniform, though that near the surface was somewhat sparse compared with the inner part. However, that of the thermally cured product was not uniform and thin films of the polymer appeared irregularly on the surface.

The rate of thermal-catalytic polymerization was determined by the percent conversion of MMA to PMMA as a function of polymerization time (Fig. 3). The bulk-MMA placed in the oven (at 80°C) commenced the polymerization within 15 minutes and reached over 95%

Table 1. The loss (wt. %) of MMA in slate during the polymerization.

	30min	1hr	2hr	3hr	8hr	16hr
Thermal-cat. polymerization	1.2	1.8	—	—	—	—
Radiation polymerization	0.8	1.3	1.7	2.3	1.2	2.6

* All the specimens are wrapped with Al-foil.

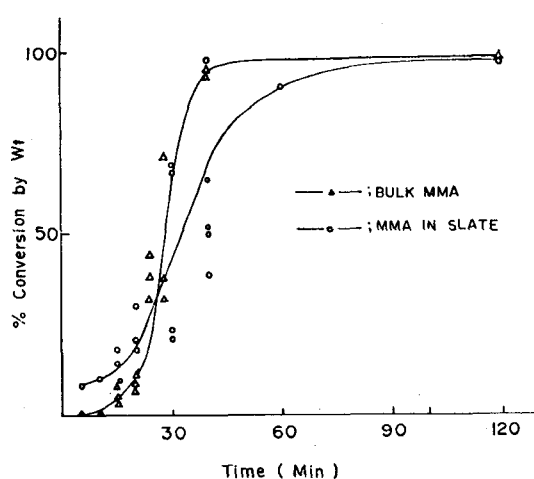


Fig. 3. Thermal-catalytic polymerization of MMA in slate (Cat.: 2.0% BPO, Temp.: 80°C)

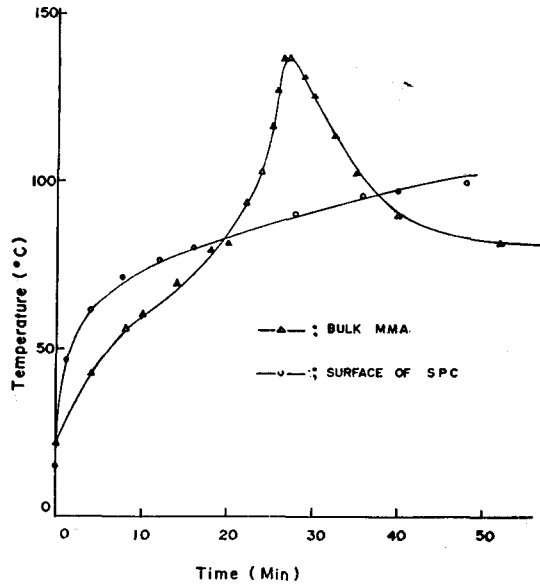


Fig. 4. Temperature change of the specimens during the thermal-cat polymerization (Cat.: 2.0% BPO, Temp.: 80°C)

conversion after 40 minutes. This result almost coincides with the data previously reported by Steinberg¹⁾. However, the MMA impregnated in the slate began to polymerize as soon as it was placed in the oven, but the overall polymerization rate was slower, and it took more than 60 minutes to reach about the same conversion %, even though the polymerization rate is almost two times faster than that occurred in the preparation of mortar-plastic composite (MPC) under the same condition⁴⁾. Consequently, we can conclude that the time needed to get complete conversion of MMA in various condition is in order of bulk < in slate < in mortar.

Above difference in the rate of polymerization may come from not only the difference in the heat transfer rate into the medium but the density of MMA in the medium where the reaction occurs, if no inhibitor of polymerization existed in the slate or mortar. The authors have determined the temperature

changes in both the surface of slate and bulk-MMA during the thermal-catalytic polymerization at 80°C (Fig. 4). It may be said that the temperature rise of the both is mainly due to heat transfer from oven under 80°C, but the higher temperature may be ascribed to the heat of polymerization. As shown in the Figure, the rate of temperature rise of the surface of slate is faster than that of bulk-MMA up to 80°C, while the latter is sharply increased after 20min. The faster temperature rise of the surface (Fig. 4) and the higher conversion % of the monomer to polymer (Fig. 3) in the slate specimen under 80°C may be attributed to its poor heat transfer compared with bulk-MMA. And also, the slower temperature rise and the lower conversion % of bulk-MMA under 80°C can be explained with its better heat transfer. The sharp increase in the temperature and conversion % of bulk-MMA after 20 min. (above 80°C) may be mainly due to the thick density of the MMA. The richness of liquid MMA may enhance the heat transfer by means of convection and induce the violent polymerization simultaneously, which emits a great amount of heat of polymerization when the specimen reaches the suitable temperature¹⁾ for polymerization. It is not yet clear which one of the two, monomer density or heat transfer property, is more effective for the overall polymerization. But it is noteworthy that the monomer in slate polymerizes more quickly than that in mortar as previously mentioned, in spite of the poor heat conductivity of slate compared with mortar. It may be due to its thicker density of the monomer in slate. The monomer loadings in slate and mortar were 17 and 10% based on the weights of the raw materials respectively.

Fig. 5 shows the rate of radiation po-

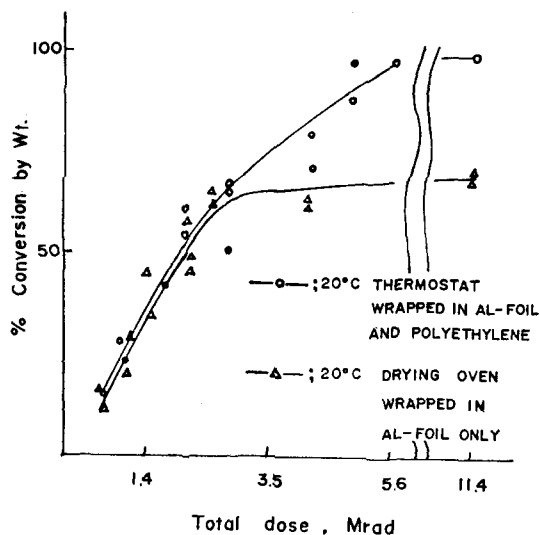


Fig. 5. Radiation polymerization of MMA in slate (Dose rate: 0.7Mrad/hr)

lymerization determined by the percent conversion as a function of total dose under the dose rate of 0.7 Mrad/hr. When the MMA-impregnated slate was wrapped in Al-foil and polyethylene film dublicately, the total dose required to obtain around 100 percent conversion was 5.6 Mrad in the thermostat maintained at 20°C. On the other hand, when it was wrapped in Al-foil only and polymerized under air, the conversion reached 65% in 2.8 Mrad but remained almost constant in spite of increasing total dose. Since the evaporation loss of the impregnated monomer during polymerization is less than 2~3% of the total, the poor result of the latter may be mainly caused by the intrusion of O₂, which is a well known free radical scavenger. The notable effect of oxygen in this case comparing with that of MPC may be due to the thin thickness of the slate specimen, in other words, the large surface which oxygen can be introduced into. The sparse polymer distribution near the surface also corroborates it.

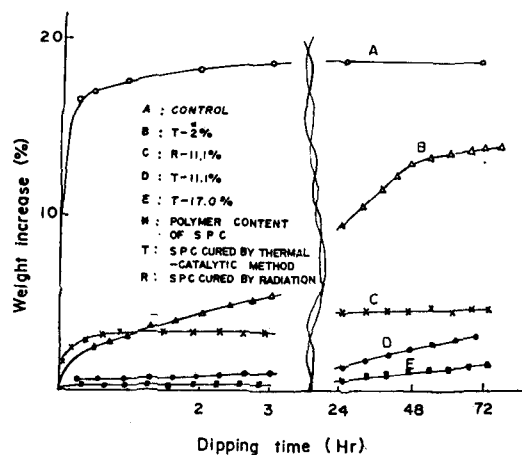


Fig. 6. Effect of polymer loading on water absorption of SPC at 20°C.

2) Properties of SPC

Fig. 6 shows the reduction in water absorption by SPC. The data indicate that the absorption is generally reduced by increased polymer content. Compared with the control's absorption of 18.4%, a considerable reduction (to 9.4% and 1.5%) was obtained after 24 hrs dipping for thermally prepared specimen containing 2.0% and 11.1% polymer. The method of initiating polymerization also seems to have some effect on water absorption; with the same polymer loading of 11.1%, thermally prepared specimen shows a better result than that prepared by radiation. This may be due to the surface film of the thermally prepared specimen. But when the water absorbed specimens reach the constant weights, both have almost the same absorption. The maximum reduction (to 2.2%) was obtained with a thermally prepared specimen containing 17.0% polymer.

Acid resistance is also proportional to the polymer loading, as Fig. 7 shows. Compared with the control's weight loss of 50%, the

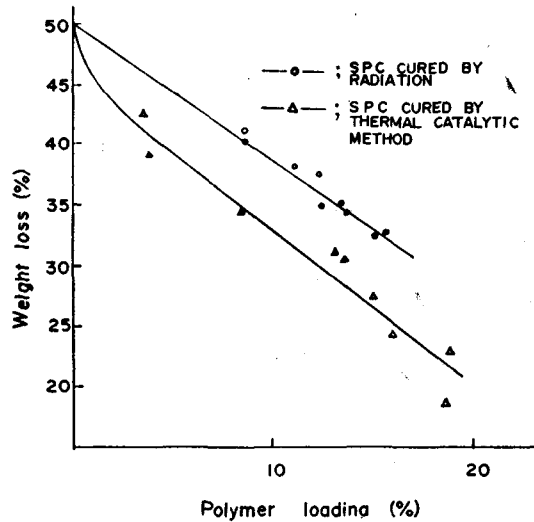


Fig. 7. Acid corrosion of SPC in 15% HCl during 48 hrs. (Temp.: 20°C)

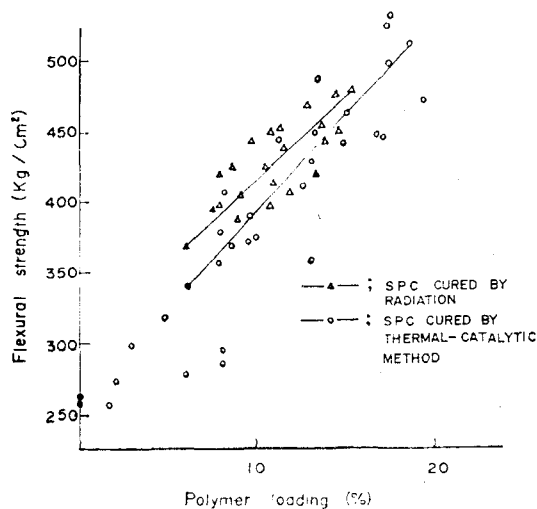


Fig. 8. Flexural strength of SPC vs. polymer loading.

test specimens showed linear decrease with the polymer loading and the maximum resistance of 22% weight loss was obtained with the thermally prepared specimen containing

18.0% polymer. Surface film of the thermally prepared specimen also gave some improvements. Although acid resistance was improved only two times in terms of corrosion resistance, it may be thought that more improvements would be observed if the strength properties of the corroded specimen were measured.

The flexural strength of specimens is plotted in Fig 8. The data indicate that the strength is generally increased by the increased polymer weight and about two times increase was obtained with the specimen containing 18.0% polymer. In contrast to the water absorption and acid resistance, the specimen prepared by irradiation showed slightly better improvement and smaller deviation than that of the thermally prepared specimen, which may be due to the homogeneous distribution of polymer in the specimen.

References

- 1) M. Steinberg, *et al.*, Concrete-polymer materials, first topical report, BNL 50134 (T-509) and USBR GEN. REP. 41, 15-20, (Dec. 1968)
- 2) M. Steinberg, Concrete-polymer material development, A goal oriented program, BNL 50313, (Oct. 1971)
- 3) Composite materials for railroad application, BNL 50371, (Feb. 1973)
- 4) Pyun, H.C., Lee, K.H., J. Korean Nuc. Soc., 2, 73-79, (1974)
- 5) 材料試験便覧, 日本材料試験協会, 797, (1957)
- 6) M. Steinberg, *et al.*, Concrete-polymer materials second topical report, BNL 50218 (T-560) and REC OCE 70-1, 7-11, (Dec. 1969)