

Effects of Formaldehyde on the Water Resistance of MDF Cement Composites

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(Received September 23, 1998)

Formaldehyde has widely been used for the cross-linking of polyvinyl alcohol polymer. The effects of formaldehyde on the water resistance of MDF cement composites were investigated as a function of types of catalyst, base or acid, and the amount of formaldehyde. The acetalization, reaction of OH group of PVA with aldehyde, was ended incompletely under base atmosphere. However, by addition of citric acid, the cross-linking of PVA polymer could be achieved through acetalization of PVA and formaldehyde. The effects of these different patterns according to the types of catalyst on the water resistance of MDF cement were studied by the preparation of PVA films and MDF composites. Thanks to the cross-linking reaction of PVA polymer chains by formaldehyde, the modified PVA films and MDF composites showed a good water-resistant property. The modified MDF cement composite to which 3 wt% formaldehyde and 1wt% citric acid were added showed 80% of initial flexural strength and good interfacial state between cement grain and polymer matrix. However, 4 wt% formaldehyde deteriorated the processing conditions, microstructures and eventually the flexural strengths, causing sharp increase in the viscosity of sample dough during the mixing process. To study the relations of flexural strength and interface of cement grain and polymer matrix, SEM and MIP measurements were performed.

Key words : MDF cement composite, Polyvinyl Alcohol, Formaldehyde, Citric acid, Acetalization, Water resistance.

I. Introduction

The cement hydrate shows much lower strength than theoretically expected strength because excessive water must be added to cement for working conditions, and cement particles tend to agglomerate, which results in highly porous structures weakened by the strength-determining macro defects.¹⁾

Based on Griffiths concept, Birchall et al.²⁾ removed the macro defects in order to enhance the strength of cementitious materials by combining hydraulic cement and water-soluble polymer in a high shear mixing process. The highly viscous, water-soluble polymer used for MDF cement plays an important role of processing aid and pore-filler. This water-soluble polymer makes it possible for cement particles to be mixed with and dispersed in polymer matrix homogeneously even under very low amount of water and for the porosity, pore size and its distribution to be reduced dramatically.²⁻⁵⁾

However, when the MDF cement composites contact water or humidity, the water-soluble polymer dissolves again and swells, resulting in low stability to water.⁶⁾ Since low water stability is a serious obstacle for MDF cement to be put to practical use, a number of investigators have studied to improve its water stability in various ways.⁷⁻¹⁰⁾

J.F. Young^{7,8)} improved the moisture resistance of MDF cement by introducing coupling effect of polymer matrix

and surfaces of cement particles and cross-linking of PVA polymer chains with silane coupling agents. J.A. Lewis⁹⁾ reported that an organotitanate cross-linking agent, Tyzor TE, modified the PVA polymer chains to improve the water stability of MDF cement. Water-resistant MDF cement was developed by incorporating anisocyanate compound into the cross-linking reaction of PVA molecules through urethane bond. Recently, dramatic improvement of water stability and strength by substituting water-soluble PVA with insoluble phenol resin was achieved by Pushipalal et al.¹⁰⁾

It has been proved that the water stability of MDF cement composites to be enhanced by the cross-linking of PVA chains. But the use of formaldehyde for the cross-linking of PVA which has widely been used in PVA polymer related industry has not been reported. So, in this work, the effects of formaldehyde on the cross-linking of PVA polymer chain and eventually the water stability of MDF cement composites are studied.

II. Experimental Procedure

1. Raw materials and composition

In this study, HAC/PVA based MDF cement composites were prepared using high alumina cement (Union Co., UAC-70, alumina content: 73 %) and 9wt% to cement weight of PVA (Shinetsu Co., PA-18S). The water content was fixed 16 wt% to cement weight. The amount of formaldehyde and

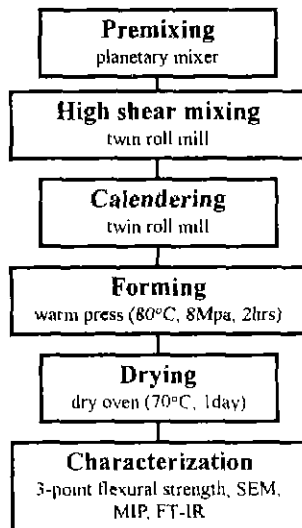
Table 1. The Composition of MDF Cement. (wt% to cement weight)

Sample	PVA	Formaldehyde	Citric acid
B1	9%	-	-
B2	9%	2%	-
S1	9%	2%	0.5%
S2	9%	2%	1%
S3	9%	3%	0.5%
S4	9%	3%	1%
S5	9%	4%	0.5%
S6	9%	4%	1%

citric acid were varied from 2 to 4 wt%, and 0.5, 1 wt%, respectively. The samples and their compositions are shown in Table 1.

2. Specimen preparation

A schematic diagram of specimen for MDF cement composite is shown in Fig. 1. First of all, the powder materials, high alumina cement and PVA were premixed for 5 minutes, followed by addition of mixed solution of water, formaldehyde and citric acid and mixed for another 5 minutes

**Fig. 1.** The flow chart of processes for MDF cement composite.

with planetary mixer. The mixture was more homogeneously mixed with twin roll mill, undergoing a high shearing while rolling speed ratio of fore and rear roll was 276:170 mm/s. Then, the dough of MDF cement composite was calendered with twin roll of equal speed. The calendered sheet was cut into the size of mold (12 × 12 cm) and then formed at 80°C under the pressure of 8 MPa for 2hrs with warm press. The demolded MDF cement composite was dried in dry oven at 70°C for 1day.

3. Characterization

The prepared plates of composites were cut into bars which were 50, 10 mm in length and width, respectively. The thickness of specimen varied from 3 mm to 6 mm according to the condition of composite in the pressing step. For estimate of water resistance, the specimens were immersed in water for 3, 7, 14 days and then, wet and dried specimens were characterized. The dried specimens were prepared in 70°C dry oven for 1day. The weight change of each wet and dried specimen was measured.

The 3-point flexural strength of specimen was tested in condition of span length, 30 mm, and cross head speed, 0.5 mm/min. The fracture surface was characterized with SEM and the porosity and pore distribution were measured by the mercury intrusion method (Autopore II 9220). The infrared spectroscopic measurements were performed in order to confirm the modification of polymer.

III. Results and Discussion

1. Acetalization of PVA

Polyvinyl alcohol is highly reactive with various kinds of aldehyde, lending itself to acetalization. The acetalization of polyvinyl alcohol is of great importance in industrial application in paints, adhesives and foams.¹¹ Both bases and acids can catalyze the acetalization, but lead to significant differences in results. As shown in Fig. 2(a), in base catalyst, carbon of formaldehyde can react with oxygen of hydroxyl group of PVA which lost the hydrogen by an effect of base, forming a carbonyl group. However, by gaining the other hydroxyl group connected to carbon of formaldehyde

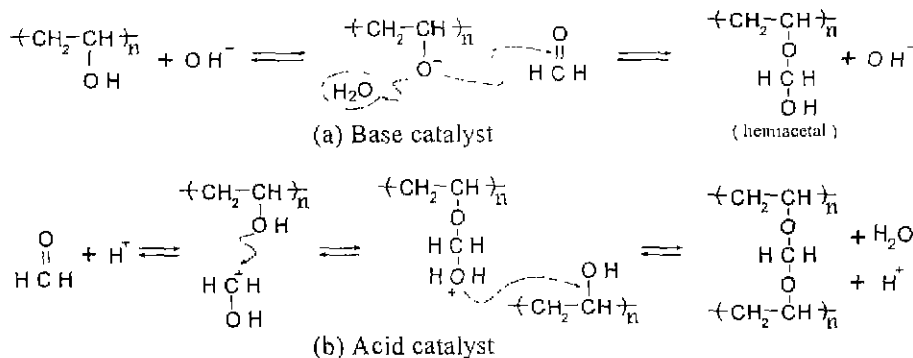
**Fig. 2.** The acetalization of PVA by formaldehyde, (a) in base-catalyst, (b) in-catalyst.

Table 2. The Composition and Dissolution Percent of PVA Film

Sample	Composition	Dissolution Percent
F-P	PVA: 100%	100%
F-PF	PVA: 80%, FA: 20%	90.2%
F-PF-Ce	PVA: 80%, FA: 20% cement water	30.4%
F-PFC-1	PVA: 85%, FA: 10% C.A: 5%	2.4%
F-PFC-2	PVA: 80%, FA: 10% C.A. 10%	7.4%
F-PFC-3	PVA: 70%, FA: 20% C.A: 10%	5.5%

attached to PVA, the acetalized PVA formed an incomplete acetal, that is, the hemi-acetal. On the contrary, an acid catalyst can protonize oxygen of hemi-acetal once more again, leading to complete acetal by reacting with an adjacent hydroxyl group. If the adjacent hydroxyl group comes from the other PVA chain, two PVA chains can be cross-linked. Therefore, in order to make PVA matrix of MDF cement composite insoluble and mechanically strong, an acid material surpassing the base of cement must be added.^{11,12)}

In this work, prior to the preparation of MDF cement composites, PVA films mixed with other materials, formaldehyde, citric acid and filtered cement water of pH 12 were

fabricated to confirm the acetalization by examination of insolubility to water. The composition and dissolution percent of PVA film in water of 50°C for 4 hrs are shown in Table 2.

The addition of only formaldehyde slightly improved the insolubility of PVA film in comparison with pure PVA film, but there was no actual difference in the state of film. Under base atmosphere of cement water(pH 12), the dissolution percent of film considerably decreased.

This improvement of water stability of PVA film achieved by base catalyst could be well evaluated. However, citric acid dramatically improved the water stability of film by catalyzing the cross-linking of PVA by the acetalization of PVA and formaldehyde. Considering that citric acid would be soluble, the value of dissolution percent of PVA films mixed with formaldehyde and citric acid represents almost 100% insolubility.

2. MDF cement composites

2.1. Strength of composites

In the preparation process of MDF cement composites, according to the formaldehyde content the work window was shortened. Because sufficient work window in high shear mixing must be essential for high strength of MDF cement composites, the deficiency of mixing time was directly reflected to the decrease of strength of composites. However, due to the improvement of mechanical property of PVA attributed by acetalization, the modified MDF cement composites showed higher flexural strength than that of pure PVA composite, except S5, S6 sample to which 4 wt% formaldehyde was added. As for the addition of citric acid, 1 wt% of citric acid made high shear mixing more difficult than 0.5 wt% in all formaldehyde content, but slightly increased the strength of composite more than 0.5 wt%. Therefore, it could be assumed that 0.5 wt% of citric acid was not sufficient to surpass the base of cement.

2.2. Water resistance

The flexural strength of the specimens of B1, B2 and S2

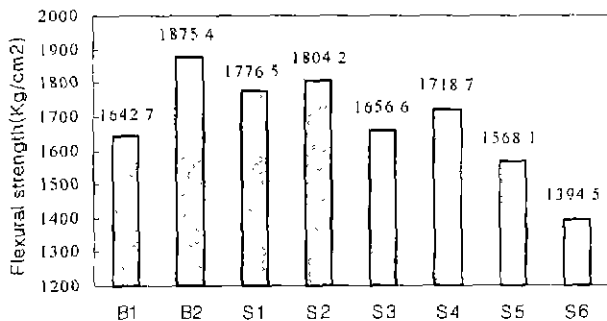


Fig. 3. The 3-point flexural strength of MDF cement.

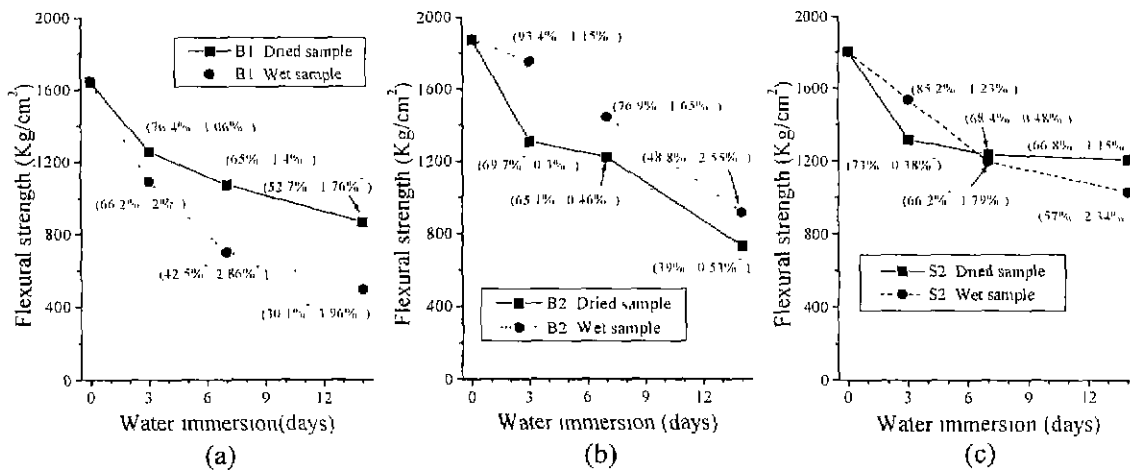


Fig.4. The flexural strength of composites which are immersed in water for 3, 7, 14 days. (a) B1: PVA 9wt%, (b) B2: PVA 9wt%, Form aldehyde: 2wt% (c) S2: PVA 9wt%, Form aldehyde: 2wt%, Citric acid: 1wt%

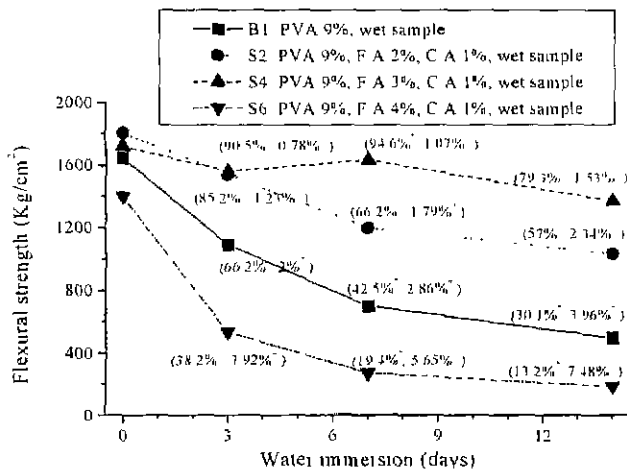


Fig. 5. The flexural strength of wet specimen of composites according to formaldehyde content.

immersed in water for 3, 7, 14 days is shown in Fig. 4. By addition of 2 wt% of formaldehyde, generally, the flexural strength of specimens was increased. However, the wet and re-dried specimens of each composite show different trends in water resistance. In case of B1 to which no formaldehyde was added, the strength of dried specimen was higher than that of wet specimen, that is, the recovery effect of re-drying was shown. On the contrary, the wet specimen of B2 maintained the 93.4% of its initial strength to 3 days in water, but the strength of re-dried specimen at 50°C for 1 day decreased to 69.7% of initial strength. This phenomenon could be accounted for by high mechanical property of modified PVA matrix in wet state. However, the specimens of B2 sample without citric acid lost the water resistance rapidly to 7, 14 days in water. This problem would be caused by imperfect acetalization in base catalyst mentioned above, which was confirmed by high water resistance of citric acid added composites, shown in Fig. 4 (c).

Fig. 5 shows the water resistance of composites according to the formaldehyde content. The specimens were tested in wet state and 1wt% citric acid was added. Although the S2 sample of 2 wt% formaldehyde showed an enhanced water resistance in comparison with B1 sample, its strength decreased steadily according to the immersion days in water.

The most water-resistant composite in this study was achieved by addition of 3 wt% formaldehyde and 1 wt% citric acid. These specimens of S4 sample retained more than 90% of initial strength to 7 days in water and about 80% to 14 days. But, in case of 4 wt% formaldehyde added, rapid increase of viscosity in preparing process deteriorated the workability and microstructure, eventually the initial strength and water resistance of S6 sample.

In this study, all immersed specimens including re-dried specimens were increased in their weights, and their strengths had a close relationship with weight gain of specimens during immersion in water. That is, the more the weight was gained, the more did its water resistance decrease. As the weight increase in water indicates the hydration of cement grain, not the dissolution of PVA matrix, these inverse proportional relations of weight gain to water resistance implied the attribution of hydration reaction of cement grain to damage of MDF cement composite in water.

2.3. Microstructure of composites

In this study, the establishment of relation between microstructure and strength of immersed specimen was attempted by the observation of fracture surface by SEM and the analysis of porosity by MIP method.

Fig. 6 shows the fracture surfaces of MDF cement composites immersed in water for 14 days. The strength of specimen was properly related with fracture pattern of cement grains and its interface with polymer matrix. As shown in Fig. 6(a), the specimen of S4 sample maintained a good condition of interface, so the crack propagated through cement grains. On the contrary, the separation of cement grain and polymer matrix was observed along with the pulled cement grains in specimen of B1 sample, shown in Fig. 6(b). So, we can obtain the assumption that the crack propagation through cement grains which is stronger than PVA matrix can imply the increase in overall strength.

In order to confirm this assumption, the analysis of pores formed by pulling of cement grains was performed with mercury intrusion porosimeter. Because MDF cement composites would be devoid of the macro pore more than 10 mm, the macro pores can be classified into the extrinsic pores generated by the pulling of cement during the fracture of

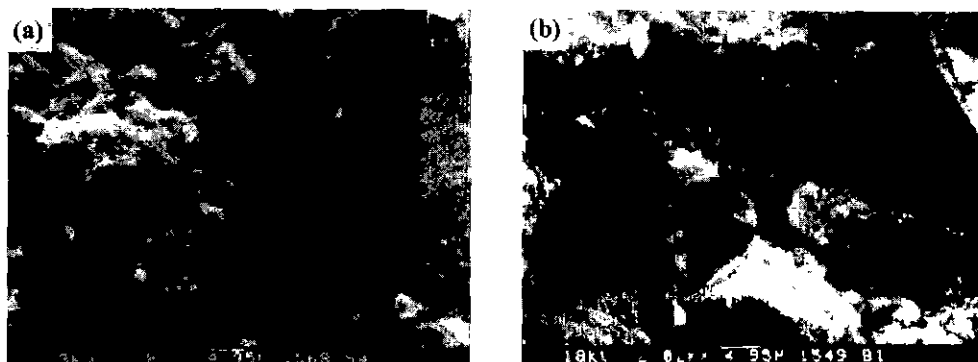


Fig. 6. Rhefracture sургaces of MDF cement composites immersed in water for 14 days. (a) S4 sample, (b) B1 sample.

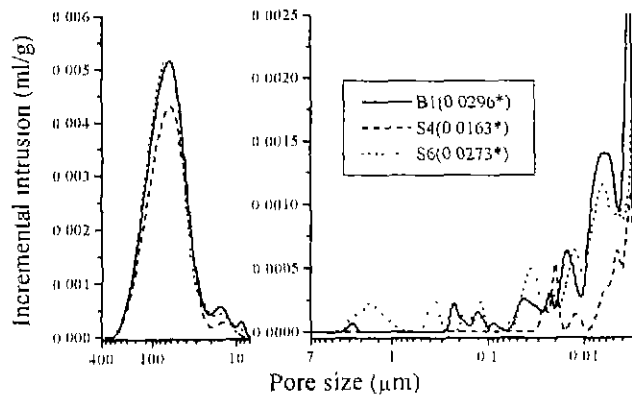


Fig. 7. pore distritions of B1 and S4 and S6 samples immersed in water for 14 days.

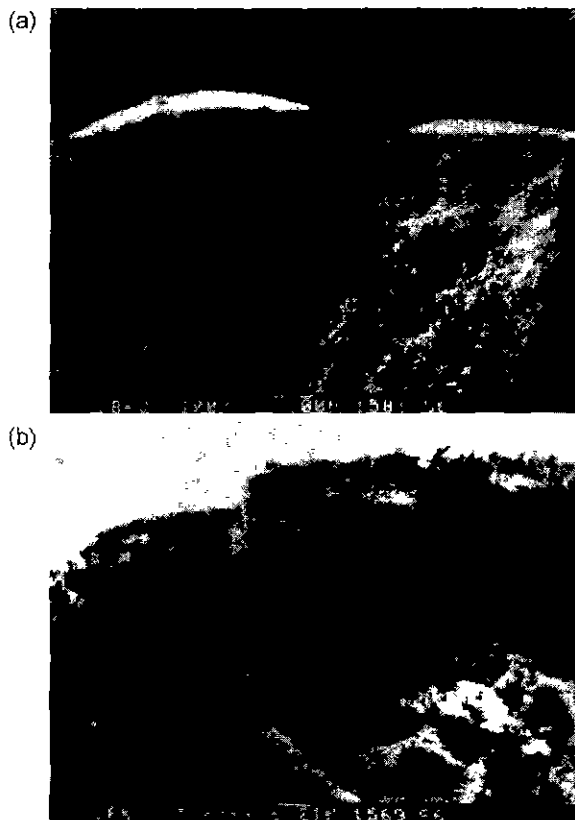


Fig. 8 The surface defects of the S6 sample.

specimen.

As shown in Fig. 7, the pore distributions of B1, S4 and S6 samples immersed in water for 14 days were compared and separated to the extrinsic pore region and intrinsic pore region with different scale. In extrinsic pore region, the increase in measured intrusion volume of specimens corresponded with the decrease of strength in their order. In addition, the distribution of intrinsic pores considered to be included intrinsically showed a reasonable pattern in comparison with their strengths.

Fig. 8 shows the surface defects of the S6 sample immersed in water. This defect appeared about 2~4 days after

specimens had been immersed in water and along with the crack toward the inside of specimen. Below the defect, there were many pores of trapped air with smooth inside surface, as shown in Fig. 8(a), which were estimated to be formed by surface defects of calendered sample, for example, the tearing defects. Moreover, dehydration and acetalization of polymer could cause the shrinkage deformation of MDF cement. So, in case of the excess amount of formaldehyde, the crack accompanied by surface defect would be caused by the trapped, pressed air bubble and shrinkage deformation, especially at weak points. This result reminds of the importance of process condition. Fig. 8(b) shows the cross and inside sections of surface defect which contains large voids and cement hydrates

IV. Conclusions

Formaldehyde made the PVA polymer insoluble by the acetalization in which polymer molecules could be cross-linked to each other. However, under the base catalyst of cement, the complete acetalization could not be achieved, with only hemi-acetal formed. As a result, the water resistance of MDF cement rapidly decreased, especially in the long-term immersion. On the contrary, the acid catalyst of citric acid made it possible for PVA polymer to be cross-linked. The modified MDF cement composites by formaldehyde and citric acid kept good water-resistant property to 7 and 14 days in water.

However, when the amount of addition of formaldehyde was 4 wt% to the cement the manufacturing process condition and microstructure were seriously deteriorated because the rapid cross-linking of PVA polymer caused sharp increase in viscosity. The optimum condition for high water resistance of MDF cement was the addition of 3 wt% formaldehyde and 1 wt% citric acid to 9 wt% PVA polymer. This modified MDF cement composite showed about 80% of initial flexural strength to the 14 days in water.

In the consideration of microstructure, the strength of MDF cement composite showed a close relationship to the interface between cement grain and polymer matrix proved by the different fracture patterns.

Acknowledgment

This work was supported by the Ministry of Trade and Industry, Republic of Korea.

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