Properties and interaction of cement with polymer in the hardened cement pastes added absorbent polymer

CHONG YOON RHA, JIN WOOK SEONG, CHANG EUN KIM
Department of Ceramic Engineering, Yonsei University, 134 Shinchon-dong, Seodaemoon-ku, Seoul, Korea, 120-749

S. K. LEE
Ssang Yong Research Center, 100 Shinsong-dong, Yusong-ku, Daejeon, Korea, 305-345

W. K. KIM
Dongyang Research Center, San 89 Jung-ri, Gusung-myun, Yongin-kun, Kyoungki-do, Korea, 440-910

Ordinary Portland cement mixed with various amounts of absorbent polymer in the form of sodium acrylate $((-CH-)_nCOONa)$ have been studied. As the content of absorbent polymer increased, heat evolution of samples decreased up to 1.15 wt % of absorbent polymer addition and conversely increased over 1.75 wt %. Flexural strength of cement paste with absorbent polymer was improved more than 20%. As the content of absorbent polymer increased, the porosity values decreased and mean pore diameter shifted to small pore diameter region. Flexural strength of ordinary Portland cement paste had a linear correlation with non-evaporable water content but, that of cement paste with absorbent polymer deviated from a linear correlation with non-evaporable water content. The chemical difference between cement pastes with and without absorbent polymer was found by the inductively coupled plasma-atomic emission spectroscopy and the infrared spectroscopy. For the infrared spectra of absorbent polymer, bands at 1416 and 1560 cm^{-1} were assigned to C—O single bond and C=O double bond respectively, namely, unidentate complex. As the curing time increased, the absorption bands near 1416 cm^{-1} shifted to longer wave number and the absorption bands near 1560 cm^{-1} to shorter wave number and finally bidentate complex was formed. Absorbent polymer released sodium ions to pore solution under the basic condition of pH 12.5–13.5 and became polyacrylic acid. Then some of these polyacrylic acid were crosslinked with others by calcium ions leached from cement grains. Calcium ion was regarded as a central charge connecting the negative parts in carbon-oxygen polarization of absorbent polymer' functional groups. © *1999 Kluwer Academic Publishers*

1. Introduction

Since the early 1900s, various polymers have been used in the field of cement and concrete for the improvement of properties that were hard to be got only with neat cement paste. Some polymers convert the electrical double layer of cement grains and act as an dispersive agent. Some polymers may form a network film in a hardened cement paste or interact with cement component hence reinforce the strength of hardened cement pastes [1]. MDF (macro-defect free) cement had been introduced by Birchall that had extremely high value of the flexural strength of cement pastes [2, 3]. Though the main factor of strength development was found to be the reduction of macro-defect of course, polymer cement interaction also became the center of interest. Several types of polymer-cement interactions

under various conditions have been reported in the literature [4–6]. The interaction between high alumina cement with polyvinylalcohol (PVA) have been attributed in some cases to a chelate of the functional groups in PVA [3]. For ordinary Portland cement (OPC), it has been reported that calcium ions leached from cement grains interacted with acrylate polymer system [7]. It was ascertained by previous literature that the complex salts were formed through the interaction of cement with polymer but, it has not been clear that the mechanism of polymer-cement interaction and the behaviors of ions in pore solution of hardened cement pastes.

The aim of this paper is to observe the effects of absorbent polymer on the cement hydration and related flexural strength. Additionally we intend to investigate the possible reaction of ions leached from cement grains

TABLE I Chemical composition of ordinary Portland cement

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Alkali	Ignition loss
(wt %)	21.48	5.29	3.03	63.31	2.80	2.45	0.072	0.873	0.80	1.16

TABLE II Physical properties of the absorbent polymers

Properties	Absorbent polymer
Appearance	White spherical powder
Average particle size	
Before absorbing	20–30 μm
After absorbing	40–90 μm
Density	
Apparent density	0.95–1
True density	1.5547 g/cm^3
Water content	~5%
pH (0.1% dispersion)	Neutral
Leaching rate (0.1% dispersion)	1%
Absorbency (times/own weight)	550–550

with carboxyl radical in hardened cement pastes containing various amounts of absorbent polymer over the time period of the experiments.

2. Experimental
Samples of ASTM type 1 ordinary Portland cement (OPC) with fineness of 3483 cm^2/g were mixed with 0.70, 0.85, 1.00 and 1.15 wt % absorbent polymer (AP) in the form of acrylic sodium salt ((−CH−)$_n$COONa) at the initial water/cement ratio of 0.30. Chemical composition of OPC and properties of AP were showed in Tables I and II respectively [8]. Distilled water was sprayed inside the rotated ball mill and the paste specimens were compacted at pressure of 30 kgf/cm^2 and then cured at 100% relative humidity (RH) and the temperature of 20 °C up to 90 days. A control sample, i.e. OPC mixed with distilled water was also fabricated. Experimental procedure was shown in Fig. 1 [9].

Mixture of absorbent polymer and cement with all composition were analyzed by conduction calorimeter (Tokyo Rico.) to estimate the heat evolution during
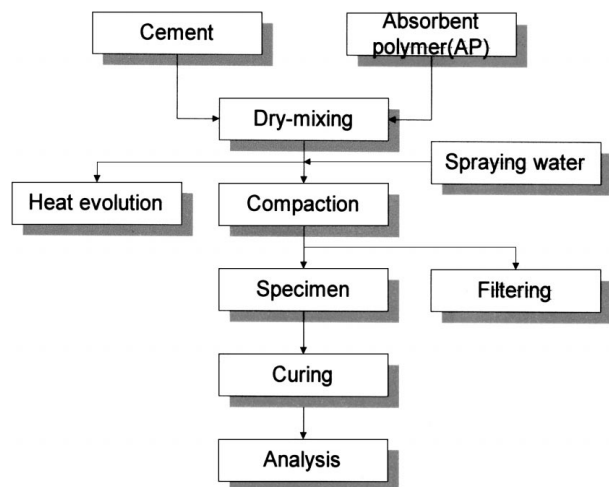

Figure 1 Flow diagram in preparation and characterization of specimens.

initial hydration. Absorbent polymer and cement were mixed with distilled water (water/cement = 1) and heat evolution amounts were measured at 23 °C and 60% relative humidity. To evaluate the effect of absorbent polymer on the degree of hydration the bound water content was calculated from the value of ignition loss. Specimens were ground and dried for 24 h at 110 °C and then treated by thermogravimetric analysis (TGA). Ignition loss was calculated from the integration of weight change before and after heat treatment.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, LABTAM 8440, Austria) specimens were prepared using a technique similar to coercive filtration by aspirator. Absorbent polymer-cement pastes was mixed with distilled water by magnetic stirrer and filtered by glass filter (pore size 0.45 μm) for 2 h. HNO$_3$ was added to solution obtained from the absorbent polymer-cement pastes. To investigate the bonding state of absorbent polymer in hardened cement pastes, specimens were analyzed by infrared spectroscopy (FT-IR, Mattson Co.). FT-IR samples were prepared using KBr method. Ground specimens were mixed with KBr at the KBr/specimen of 100 and compacted to disk type pellets. Transmittance of the samples was measured from 400 to 4000 cm^{-1}.

3. Results and discussion
Figs 2 and 3 give isothermal calorimetry curves showing rates of heat evolution as a functions of time for
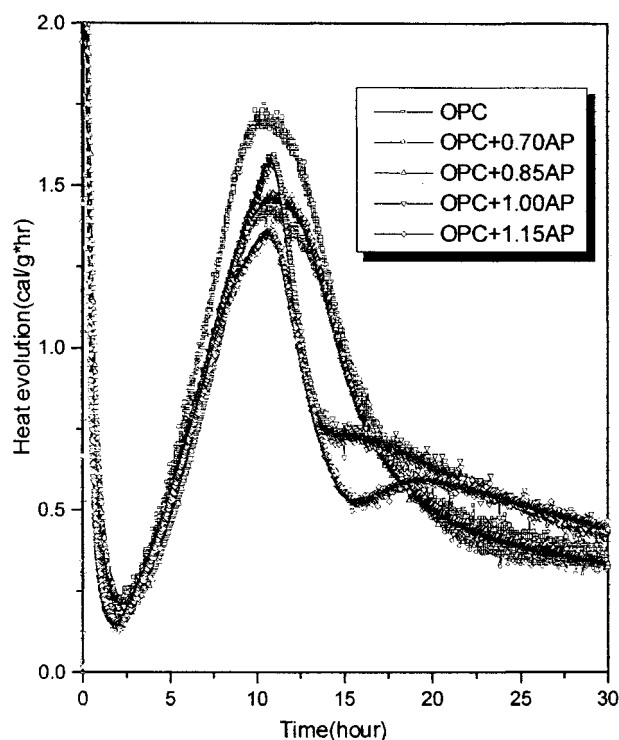

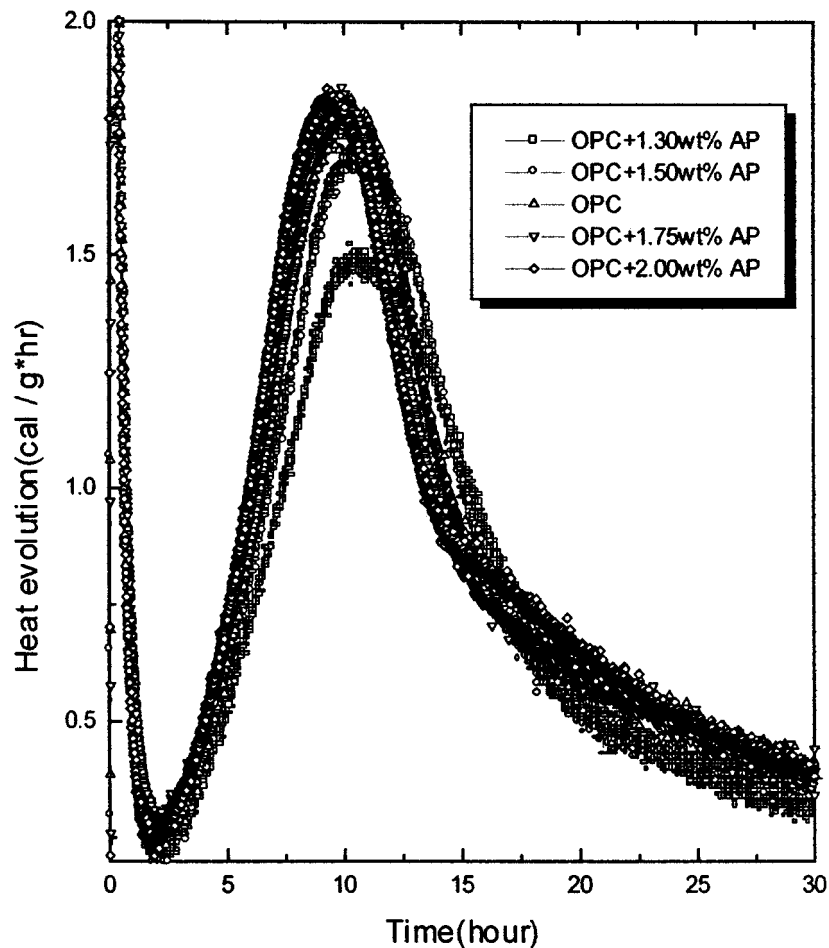*Figure 2* Heat evolution of absorbent polymer-cement paste during 30 hours.

Figure 3 Heat evolution of absorbent polymer-cement paste during 30 hours.

ordinary Portland cement and absorbent polymer added ordinary Portland cement at water/cement = 1.0 during the first 30 h of hydration. Heat evolution of absorbent polymer added ordinary Portland cement decreased up to 1.15 wt % of absorbent polymer addition. To the contrary, heat evolution of absorbent polymer added ordinary Portland cement increased from 1.15 wt % of absorbent polymer content and exceeded that of ordinary Portland cement over 1.75 wt % of absorbent polymer content. It is noted that, until recently, it was widely believed that there were two types in that various polymers affected the hydration of ordinary Portland cement [1]. The one is an accelerator type and the other is a retarder type.

But, it was observed that absorbent polymer acted as both of an accelerator and a retarder rather than classified into one type. When absorbent polymer was added to ordinary Portland cement below the content of 1.5 wt %, it was considered that the reduction of nucleation probability required to cement hydration caused the reduction of heat evolution because absorbent polymer attracted the ions leached from cement grains near absorbent polymers. For the case of absorbent polymer addition over 1.75 wt %, it was considered that the effect of alkali activation on cement hydration by Na ions dissolved from absorbent polymer could preferably increase the heat evolution [8].

The variation of non-evaporable water content calculated from thermogravimetric analysis in the presence

of absorbent polymer are shown in Fig. 4 [10] and the results of the flexural strength as the function of the degree of hydration are shown in Figs 5–8. As the hydration progressed, the values of the non-evaporable water content increased in all the cases. The values of non-evaporable water content were highest for the control (OPC), lowest for the cement containing 1.15 wt % absorbent polymer. This figure clearly shows that as the amount of absorbent polymer, the extent of hydration decreased but difference of the values between at 56 and 90 days is far pronounced. It is considered that the release of remnant water from absorbent polymer could develop the long-term hydration [10]. The flexural strength of the control (OPC) increases continuously with time. These values are increased further in the presence of absorbent polymer. Higher the amount of absorbent polymer, greater is the flexural strength. The degree of hydration of the control corresponds linearly to its flexural strength but as the content of absorbent polymer increases, the relationship between both parameter of the cement pastes containing absorbent polymer is showed less linear. So, the variation of non-evaporable water content is not in support of this observation. It appears that the homogeneity at mixing stage is more important than the degree of hydration under the low water to cement ratio. In order to know the effect of porosity on the flexural strength of the cement pastes, pore size distribution of the control (OPC) and in presence of absorbent polymer were determined (Fig. 9).
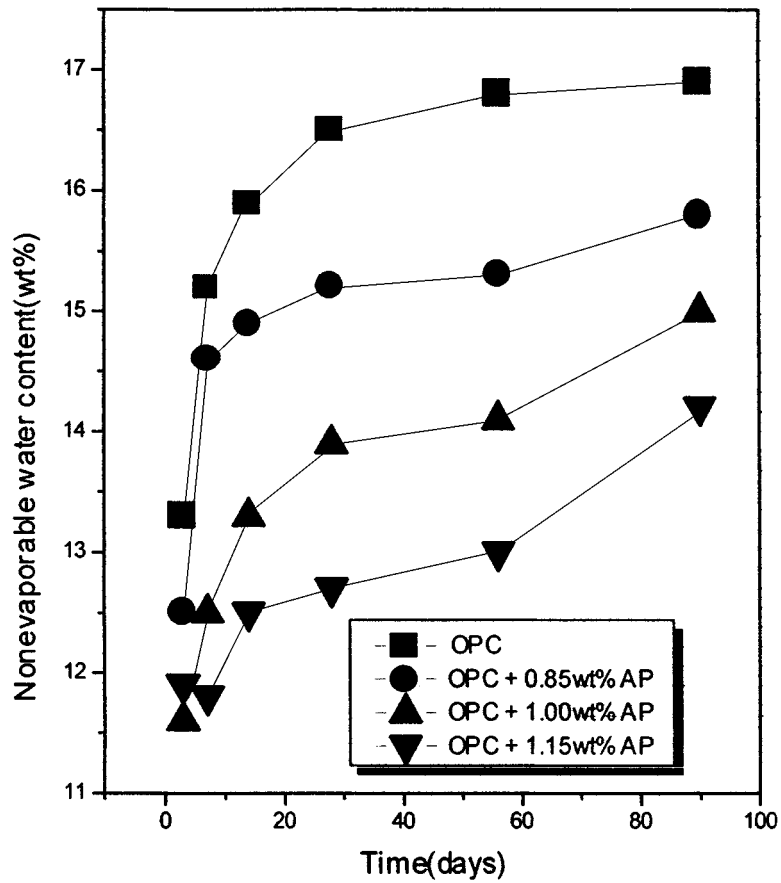
Figure 4 Non-evaporable water content of absorbent polymer cement pastes.
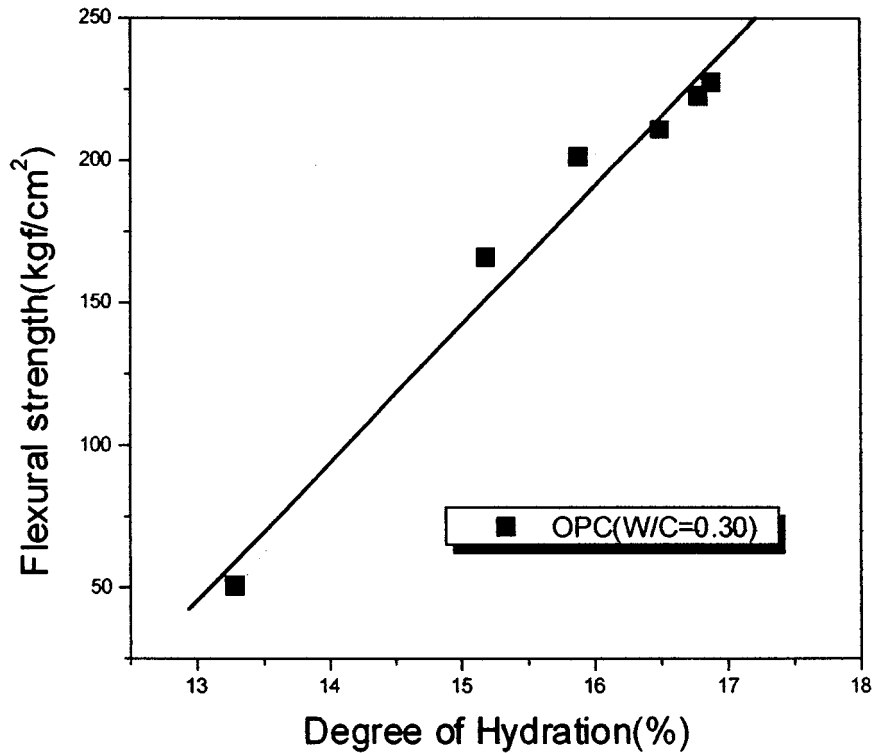

Figure 5 Flexural strength of ordinary Portland cement paste as a function of degree of hydration.

As the content of absorbent polymer increased, the porosity values decreased and mean pore diameter shifted to small pore diameter region. This results explain successfully above flexural strength and correspond to other reports.

Fig. 10 shows various ions concentration in 3 different solutions by inductively coupled plasma-atomic emission spectroscopy (ICP). The value of calcium ion concentration in solution leached from cement paste and in that solution leached from absorbent polymer
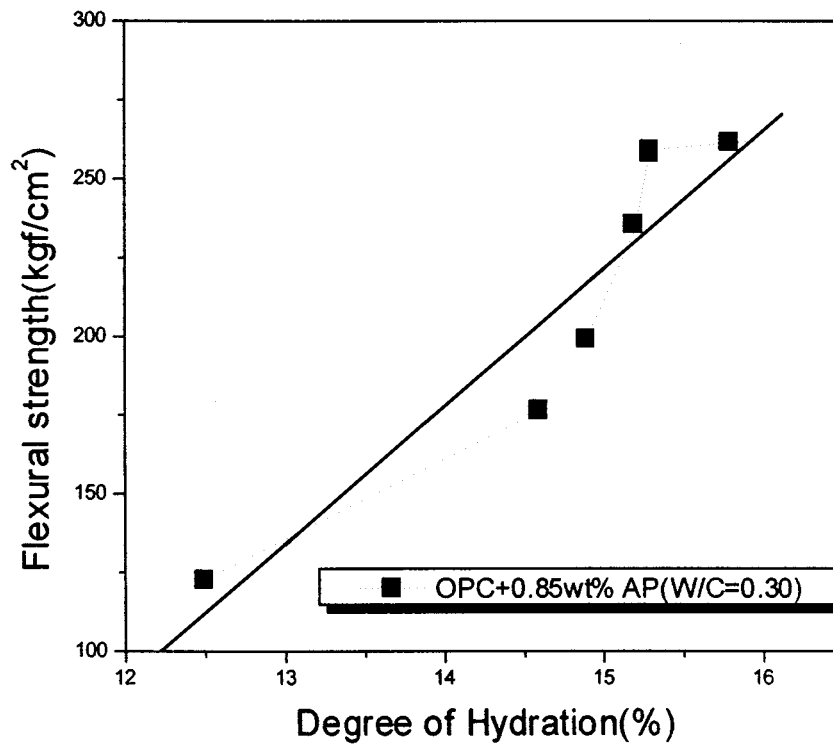
Figure 6 Flexural strength of ordinary Portland cement paste with absorbent polymer as a function of degree of hydration.
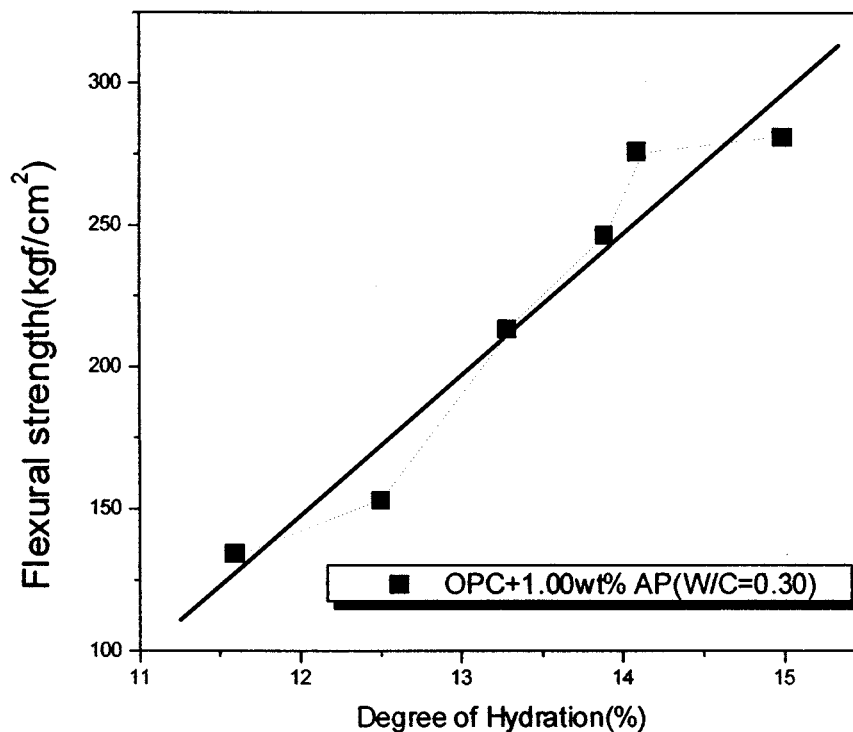

Figure 7 Flexural strength of ordinary Portland cement paste with absorbent polymer as a function of degree of hydration.

gel are 390 and 50 ppm respectively. If there is not any interaction between cement and absorbent polymer, the theoretical value of calcium ion concentration in solution leached from cement-absorbent polymer paste will show 220 ppm as average value. But, the experimental value of calcium ion concentration in solution leached from cement-absorbent polymer paste shows 90 ppm and this value is much lower than the theoretical value. This means that the interaction between cement and absorbent polymer which is more strong than the coer-

cive filtering pressure exists [9]. The infrared spectra of cement pastes with and without absorbent polymer are given in Figs 11 and 12 respectively. Band assignments are based on the standard texts by Bellamy [11] and Nakamoto [12], and general literature. Bands of particular importance to the present study were the carbonyl C=O stretching mode and C—O asymmetric stretching mode of the carcoxylic acid group. The asymmetric and symmetric CO_2^- stretching modes are growing prominently in the spectra of the control (OPC) according
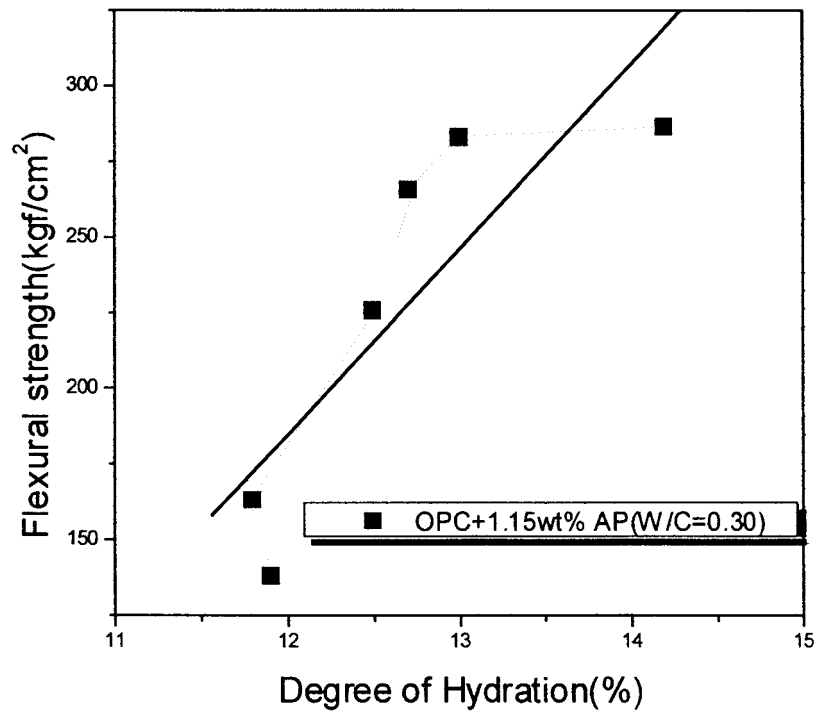
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Figure 8 Flexural strength of ordinary Portland cement paste with absorbent polymer as a function of degree of hydration.
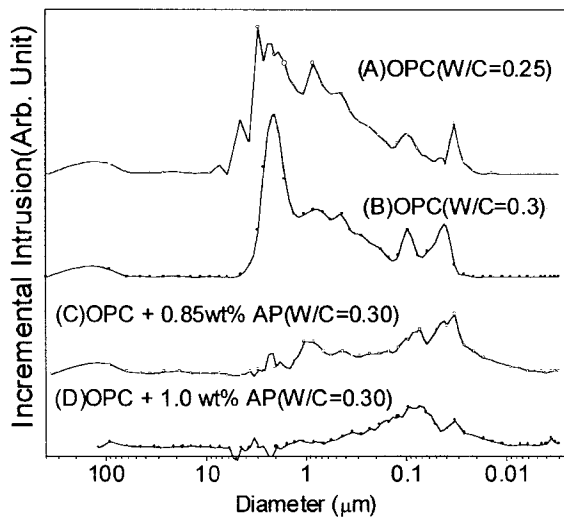

Figure 9 Pore size distribution of cement paste with and without absorbent polymer.
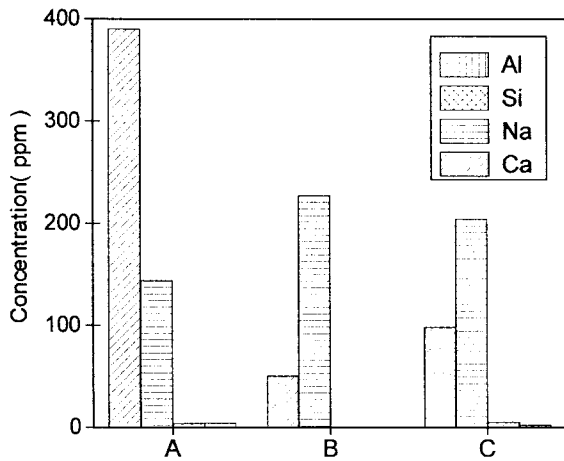

Figure 10 Leaching amounts of ions in coercive filtered solution. (A) Leached cement solution, (B) Leached absorbent polymer solution, (C) Leached cement-absorbent polymer solution.
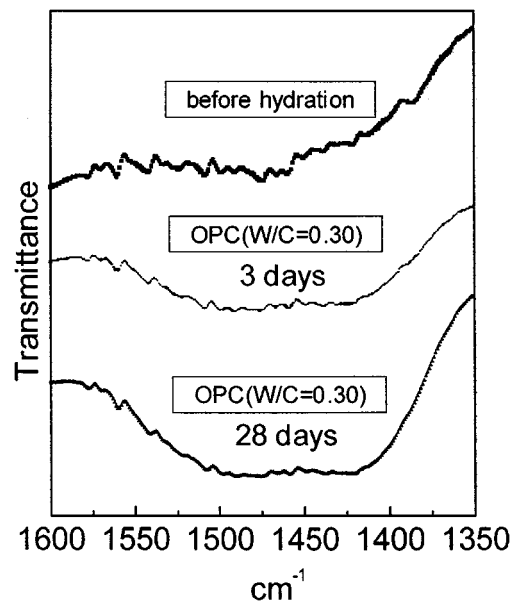

Figure 11 Infrared spectra of ordinary Portland cement paste as a function of time.

to time. For the infrared spectra of absorbent polymer, bands at 1416 and $1560 \, cm^{-1}$ were assigned to C—O single bond and C=O double bond respectively, namely, unidentate. As the curing time increased, the absorption bands near $1416 \, cm^{-1}$ shifted to longer wave number and the absorption bands near $1560 \, cm^{-1}$ to shorter wave number and finally bidentate was formed. It is considered as follows. Absorbent polymer released sodium ions to pore solution under the basic condition of pH 12.5–13.5 and became polyacrylic acid. Then some of these polyacrylic acid were crosslinked with others by calcium ions leached from cement grains. Calcium ion was regarded as a central charge connecting the negative parts in carbon-oxygen polarization of
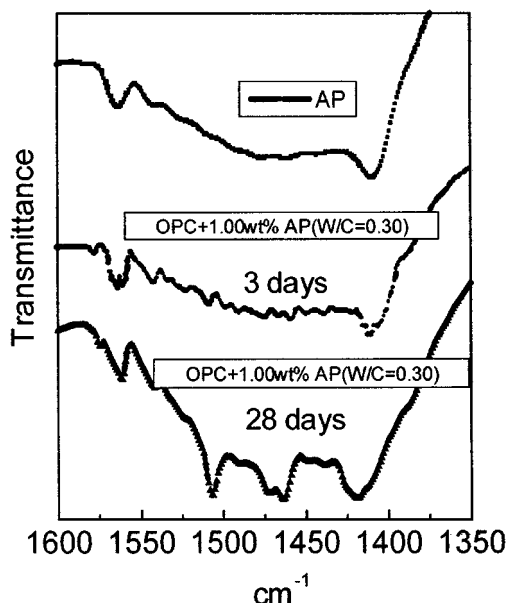
Figure 12 Infrared spectra of ordinary Portland cement paste with absorbent polymer as a function of time.

absorbent polymer' functional groups. The unidentate complex (absorbent polymer) as starting material converted to the bidentate(chelate) complex [6].

4. Conclusions
Ordinary Portland cement paste mixed with various amounts of absorbent polymer in the form of sodium acrylate (($-CH-$)$_n$COONa) have been studied and from above results, following conclusions have been made.

(1) Absorbent polymer in hydration behaviors of ordinary Portland cement pastes acted as a retarder below the addition content of 1.15 wt % and an accelerator over 1.75 wt %.

(2) Flexural strength of cement paste with absorbent polymer was improved more than 20%. Strength development did not depend on non-evaporable water content but pore size distribution. As the content of absorbent polymer increased, the porosity values decreased and mean pore diameter shifted to small pore diameter region

(3) For the infrared spectra of absorbent polymer, bands at 1416 and 1560 cm^{-1} were assigned to C$-$O

single bond and C$=$O double bond respectively, namely, unidentate complex. As the curing time increased, the absorption bands near 1416 cm^{-1} shifted to longer wave number and the absorption bands near 1560 cm^{-1} to shorter wave number and finally bidenate complex was formed. Absorbent polymer released sodium ions to pore solution under the basic condition of pH 12.5–13.5 and became polyacrylic acid. Then some of these polyacrylic acid were crosslinked with others by calcium ions leached from cement grains. Calcium ion was regarded as a central charge connecting the negative parts in carbon-oxygen polarization of absorbent polymer' functional groups.

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