Poly Acrylic Acid Ethyl Acrylate as Smart Carrier for Rebar Inhibitor Delivery in Alkaline Condition

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***Abstract*—With ethyl acrylate, acrylic acid as monomers, an intelligent carrier material (PAE) was synthesized, and its swelling properties at different pH values, its cycle characteristics as well as its release control performance for inhibitors in alkaline solution were studied. The results indicate that the synthesized material is sensitive to pH and has excellent cycle performance which is suitable for controlling drug delivery in the pH range from 10 to11.**

Keywords-acrylic acid; ethyl acrylate; pH sensitivity; drug delivery; rebar inhibitor

I. INTRODUCTION

Reinforced concrete structures are widely used in various construction fields by virtue of their excellent structural performance and durability [1]. However, corrosion of reinforcement has induced many instances of premature failure of reinforced concrete components world-wide [2, 3]. It has been reported that rebar corrosion occurs only when the pH of the environment is decreased to or below11.The degradation of concrete structure due to steel rebar corrosion has become a serious problem and resulted in heavy socio-economic burden for many industrial departments. Application of corrosion inhibitors during the concrete casting process is always considered to be an effective and economical solution and has been used in more and more countries [4, 5]. However, the waste of resources is a big problem during the application process of rebars inhibitors. On the other hand, some traditional inhibitors have an adverse affect on the environment. Therefore, to control the delivery of rebar inhibitors has an important economic and practical sense and this can be achieved by using pH sensitive materials. Investigations by Yang Yuxia [6] have indicated that poly acrylic acid derivates has pH sensitivity and are potential inhibitor carrier. Thus, in the work described in this paper, a polymer using poly acrylic acid and ethyl acrylate as monomers was synthesized and its pH sensitivity, cycle characteristics and rebar inhibitor delivery control properties in alkaline media was investigated.

II. EXPERIMENTAL

A. Preparation of poly acrylic acid ethyl acrylate(PAE)

The acrylic acid and ethyl acrylate monomers with the ratio of 1:1 were dissolved in anhydrous ethanol. Then distilled water, crosslinking agent, namely, N, N '-methylene bisacrylamide and the initiator $NaHSO_3$ was added into the reactor, mixed uniformly and sealed in the reactor for 24h in an water bath with the temperature of 25 ℃. The prepared polymer was taken out of the reactor and washed 3 times with distilled water to remove unreacted, crosslinking agent and initiator, then it was cut into thin slices after immersion in the distilled water at room temperature for 12h, Finally, the dried polymer was placed in a drying oven with the temperature of 50 ℃to constant weight for experimental use.

B. Solution preparation

The buffer solutions with the pH values of 7 and 8 were prepared by 0.2mol/L Na_2HPO_4 solution and 0.3 mol/L NaH_2PO_4 solution, the one with the pH value of 9 was prepared with 0.05mol/L borax solution and 0.2mol/L solution of boric acid. 0.1mol/L Na_2CO_3 solution and 0.1mol/L $NaHCO_3$ solution configurated buffer solutions of pH 10 and 11.Saturated $Ca(OH)_2$ solution was used to be the solution of pH 12.6.The solution with the pH value of 1 was prepared by diluting concentrated hydrochloric acid. All the pH values of the solutions were determined using PHS-25 digital pH meter accurately.

C. Determination of the equilibrium swelling ratio

The equilibrium swelling properties could be determined by weight method. After immersion in the buffer solutions of different pH for 7 days, PAE samples were taken out of the solutions and the moisture on their surfaces were removed with filter paper. In this case, the wet weight could be obtained by weighing the sample and noted M1. Then the sample was put into the drying oven to constant weight at 50 ℃,and the dry wet could obtained, namely, M2. Then according to the equation SR= (M1-M2) /M2 × 100(%), the equilibrium swelling properties could be measured.

D. Electrochemical experiments

The carbon steel samples (Ø 8 mm × 10 mm) were prepared by the same steel rebar (0.15% C; 0.15% Si; 0.44% Mn; 0.30% P; 0.03% S and balance Fe). Except for an exposed area of 0.502 cm^2, the rest part was embedded in epoxy resin. Prior to experiments, all specimens were gradually ground with emery paper to 800 grit. Before the electrochemical measurements, the carbon steel samples were classified to three group and respectively immersed in three types of saturated $Ca(OH)_2$ solution of which the pH was adjusted to 11 using $NaHCO_3$.The three types of solutions were: blank (with no inhibitors); with rebar inhibitor or with PAE carrying rebar inhibitor. The amounts of rebar inhibitors employed were both 0.1mg/L. Electrochemical tests were performed on the Parstat 2273 system (Princeton Applied Research) facilitated with a three-electrode jacketed test instrument. A large platinum plate was used as counter electrode. The reference electrode was saturated KCl calomel electrode. The electrochemical impedance spectra were collected in the frequency range 100 kHz to 10 mHz at the OCP using a 10 mV sinusoidal potential perturbation.

All the experiments were carried out at room temperature and all the reagents used are of AR degree.

III. Results And Discussion

A. *pH sensitivity tests*

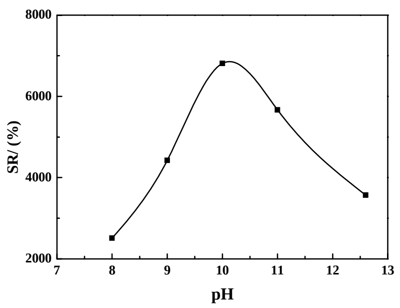

Figure 1. SR of PAE in solutions with different pH values

Fig.1 shows the SR evolution of PAE with the pH. It is clear that PAE is sensitive to pH in alkaline environment. At low pH range, the SR of PAE increased with the increasing pH value which is ascribed to that the dissociation degree of -COOH groups are increased with increasing pH value, and cause the negative charges increasing in the polymer chain, thus, its volume increases with the increasing pH value due to the electrostatic repulsion.[7] However, when the pH value is higher than 10, all the -COOH groups have been dissociated, meanwhile, the cations gathered in the negative polymer chain increase with the increasing pH due to the Coulomb effect and the electrostatic repulsion of the polymer chain is weakened, leading to the decrease of SR. The pH sensitive properties of PAE entitle it to be an excellent carrier material for rebar inhibitor delivery control. In the initial stage when the concrete is casted, the pH value of the service environment is 12-13, and the volume of the PAE is small that the rebar inhibitor is wrapped in the carrier. However, when the pH value of the concrete decreases to 11, the rebar inhibitors can be released and suppress the initiation of steel rebar corrosion, thus, the inhibition effect of rebar inhibitor can be maximized.

B. *Cycle performance determination*

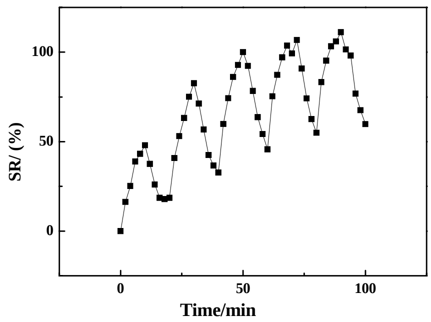

Figure 2. Dynamical change of PAE in solutions of pH=1 and pH=12.5.

In order to test the usability and stability of PAE, cycle performance determination were conducted by measuring the weight of PAE in the solutions of pH=1 and pH=12.6 alternately. Firstly, PAE was put in the hydrochloric acid solution of pH=1, and the weight of PAE was measured each 2 min. 10 minutes later, then it was transferred to the saturated $Ca(OH)_2$ solution with the pH value of pH= 12.6. These processes were repeated until 100 min. Then the swelling dynamical change of PAE could be obtained, as shown in Fig.2. It can be seen from Fig. 2 that PAE is shrinking in acidic medium and is swelling in alkaline environment. As analyzed previously, it is related to ionization of -COOH groups[6,7]. The cyclic tests showed that the pH response properties of this material exhibit good reproducibility, however, the overall SR showed an increasing trend due to the long equilibrium swelling time. Yet, the excellent reproducibility of the swelling performance of the material at different cyclic period has suggested that PAE is very stable and its pH response properties can be reversible.

C. *Rebar inhibitor delivery control properties of PAE*

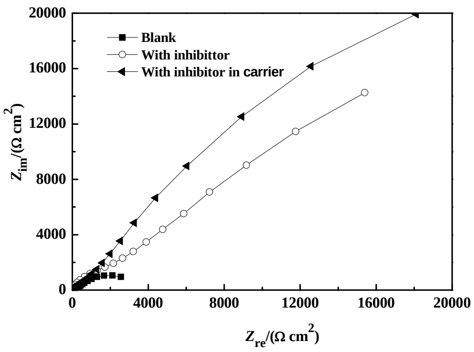

Figure 3. Electrochemical impedance spectra (Nyquist plots) of carbon steel samples in different solutions

Fig. 3 depicts the electrochemical impedance spectra of the steel electrodes in different solutions. It is notable that the capacitive arc radius of the steel sample immersed in the blank solution is very small, indicating the sample suffers serious corrosion. However, for the systems either with rebar inhibitor or with PAE carrying rebar inhibitor, the capacitance arc radius of the steel samples are much larger, which are both one order of magnitude greater than the blank one, indicating the corrosion resistances of steel samples are significantly enhanced by the inhibitor. These results should be ascribed to that the inhibitors can be adsorbed on the steel surface and form a protective layer which inhibited the corrosion of the steel samples. [8, 9] Furthermore, compared to the steel sample in the system only with rebar inhibitor, the capacitance arc radius of the steel sample is larger in the system with PAE, illustrating the excellent rebar inhibitor control properties of PAE.

IV. CONCLUSIONS

A pH sensitive smart material was prepared using acrylic acid, acrylate as monomers. The synthesized material is very stable and has excellent cycle properties, which is suitable for controlling drug release in the systems that dug delivery is in the range from10 to11. Electrochemical experiments confirm its effectiveness in controlling rebar inhibitor releasing.

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