Controlling Degradation and Physical Properties of Chemical Sand Fixing Agent-Poly(aspartic acid) by Crosslinking Density and Composites

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ABSTRACT: Poly(aspartic acid) (PASP) hydrogel crosslinked with 1,6- hexamethylene diamine was applied as sand fixing agent. The effect of crosslinking density of sand fixing agent on sand fixing property was studied. The relations between the degradation time and crosslinking density, sand fixing property, molecular weight, and mass loss were measured. It was found that the sand fixing property relied on the PASP crosslinking density and degradation time. The crust attained the maximal mechanical strength when the PASP crosslinking agent concentration was 0.0325 mol/L and the PASP hydrogel mass loss was 97.9% after 18 days. The composites added into PASP could increase mechanical property and prolong the degradation time when compared with the control. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1557–1563, 2009

Key words: poly(aspartic acid); hydrogels; degradation; sand-fixing agent; crosslinking density

INTRODUCTION

Hydrogels have been widely applied as biomedical and water retention materials in pharmaceutical and agricultural fields.[1–4] One of concerns of these materials is biodegradability in human body and natural environment. The products made from biodegradable materials do not require additional measurements to remove them. Although some important water-soluble polymers, such as poly(acrylic acid), poly(methacrylic acid) may cause pollutions to environment, so the biodegradability of biomaterial is important.

The biocompatibility and biodegradation of poly (amino acid) make them ideal candidates for many applications in detergent, cosmetics, biomedicine, and horticultural fertilizer.[5,6] Poly(aspartic acid) (PASP), belonging to the family of chemical synthetic poly(amino acid) with free carboxylic groups on chain, is a biodegradable water-soluble polymer.[7,8] It is synthesized by thermal polycondensation of aspartic acid and ammonium salts of maleic acid to form polysuccinimide (PSI). In our earlier research, the crosslinked PASP was applied as chemical sand fixing agent and three aging tests were carried out to measure its sand controlling property.[9] The critical properties of the sand fixing agent include degradation time and mechanical strength: (1) the material should not degrade completely before the crust forming, and (2) the sample with good physical properties (compressive strength and wind erosion resistance) could withstand kinds of aging tests. Specially, the main purposes of this article included: (1) the relation between cross-linking density of sand fixing agent and its mechanical strength, and (2) the effect of composite on sand fixing property. The mass loss, hydrogel crosslinking density, sand fixing properties (compressive strength and wind erosion modulus), and molecular weight of degraded fragment as function of degradation time were measured. The loss of sand fixing mechanical property during degradation process was interpreted in the term of change in polymer crosslinking density by the Flory-Rehner equation.

Total N (mg/g)	Total P (mg/g)	K (µg/g)	Organic matter (mg/g)	Biomass (µg Chla/cm^2)
0.35 ± 0.02	0.45 ± 0.02	10.2 ± 0.50	12.1 ± 0.40	0.65 ± 0.03

MATERIALS AND METHODS

Materials

L-aspartic acid, xanthan gum (2.1×10^6), and κ-carrageenan (3.4×10^5) were all obtained from Beijing chemical reagent company (China). N,N-Dimethylformamide (DMF), phosphoric acid, and 1,6-hexamethylene diamine (HD) were used without any further purification. The concentration of NaOH solution was adjusted to 27 wt %. The sand sample was taken from Fangshan Country National Natural Forest Resource Protective Engineering District, Shanxi Province, China (43°42′ N, 13°25′ E), and the sand element analysis was shown in Table I.

Preparation of PSI and PASP hydrogel

L-aspartic acid(2 mol) and 85% phosphoric acid (1 mol) were mixed at room temperature, and the mixture was heated to 210°C for 4.5 h in a kneader under a vacuum of 0.09 MPa. The product was washed with water until neutral and then dried at 85°C under a vacuum of 0.09 MPa. Finally, the powder of PSI with molecular weight of 199,500 Da was obtained.

The precursor polymer, 0.97 g of PSI (0.01 mol of succinimide monomer unit) was dissolved in 28-mL DMF in a 250 mL beaker with a magnetic stirring, and 8-mL deionized water as a dispersant was added into the beaker. The mixture containing PSI, DMF, and deionized water was stirred for 0.5 h, and then 0.0005 mol 1,6-hexamethylene diamine used as crosslinking agent was added into the beaker. The crosslinking reaction was carried out for 1 h at 40°C.

After the crosslinked polymer was formed, the imide rings of the crosslinked polymer were hydrolyzed with 27 wt % NaOH at 40°C until pH 9. Then 100-mL ethanol was added, and the precipitate was dried by vacuum drying at 40°C for 48 h. Thereby, the crosslinked PASP resin was obtained (Fig. 1). For PASP composites synthesis, certain amount of xanthan gum and κ-carrageenan were added to the beaker before the crosslinking reaction and the following process were the same above.[10]

Sand sample preparation, mechanical property, and hydrogel swelling measurement

The sample treated with PASP was prepared by following way: certain amount of sand, PASP, and tap water were mixed to form three components mixture. The mixture was cast into mold (2 cm in height and 6 cm in diameter for compressive strength test and 6 cm in length, 8 cm in width, 15° in angle of wedge-shape for wind erosion test) and was placed in an oven at 80°C for 24 h until the cementing sand was formed.[9]

There were two parameters to evaluate the effect of sand-fixing property: compressive strength and wind erosion modulus. The compressive strength was determined by press machine purchased from Beijing JianQiang Instrument Company, China: the strength was loaded on the central of the sample until cracks appeared and the value was recorded as compressive strength. The wind erosion modulus was measured in a portable wind tunnel: it was a low-speed, straight closed-throat wind tunnel. An axial fan with a diameter of 0.18 m and six blades
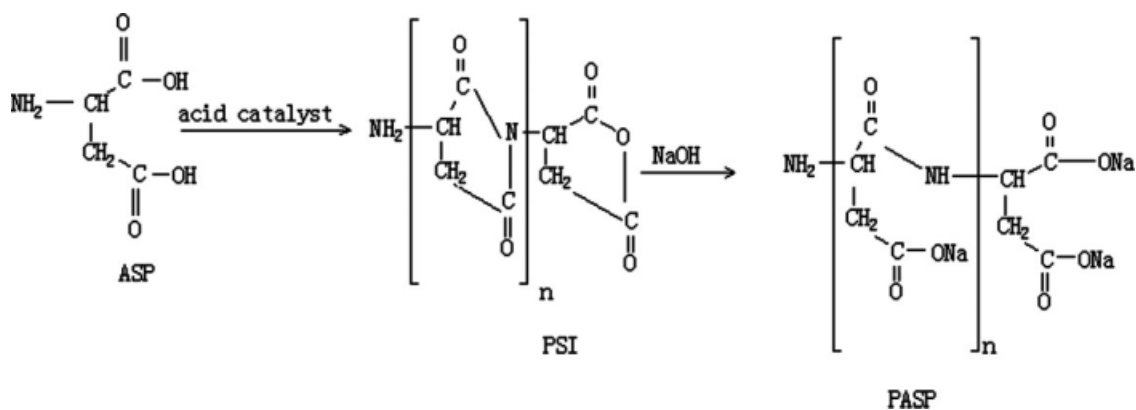

Figure 1 Preparation of PASP.

were driven by a 0.3 KW electric motor mounted at the front of the wind tunnel. The sample was placed on the flat that under 1 cm from the central line of tunnel and was 90 cm from the fan. The weight of sand loss under each test was calculated by comparing the weight difference before and after a test. The weight loss in grams was converted to the erosion modulus [g/(m^2 min)].[9]

The hydrogel swelled in deionized water and the swelling ratio was measured by the tea-bag method.[10] The degree of swelling ratio (Q) was defined as reciprocal of volume fraction of the polymer (v_2):

$$Q = v_2^{-1} = [1/\rho_p[(Q_m/\rho_s) + (1/\rho_p)]^{-1}]^{-1} \quad (1)$$

where ρ_p was the density of polymer (1.20 g/cm^3), ρ_s was the density of water (0.9970 g/cm^3 at 25°C), and Q_m was the swelling ratio, defined as the weight ratio of swollen and dried gel.

Determination of crosslinking density

According to Flory-Rehner equation, the following equation could be attained when the hydrogel in swelling equilibrium state,

$$M_C = \frac{-[ln(1 - v_2) + v_2 + \chi_{12}v_2^2]}{(v_2^{1/3} - 2v_2/f_A)} \quad (2)$$

where χ_{12} was the polymer—solvent interaction parameter, v_2 was the volume fraction of polymer in the swollen gel, f_A was the fraction of ionic units in the polymer ($f_A = 2$ in the current study), and M_c (mol/cm^3) was the molecular weight of polymer chains between two successive crosslinks. The value of χ_{12} could be measured by Flory-Huggins equation:

$$\frac{\Delta\mu_m}{RT} = -ln(1 - v_2) + v_2 + \chi_{12}v_2^2 \quad (3)$$

where $\Delta\mu_m$ was the standard chemical potential.

Degradation in field

The weighted sand fixing agent was enclosed in a 250 mesh tea-bag and buried in soil mentioned above and the water content in soil was 5 wt %. At regular time intervals, the sample was taken back to laboratory and the weight loss, swelling ratio, and gel crosslinking density were determined. The sample degradation time was defined as the time needed to total degradation ($W_t = 0$) and the degree of degradation was calculated by following equation:

$$masslost = \frac{W_i - W_t}{W_i} \quad (4)$$

where W_i and W_t was the weight of the sample at initial and at specified time during the degradation process.

Gel permeation chromatography (GPC) analysis of degraded fragment

The molecular weight of fragment degraded from PASP was measured by gel permeation chromatography with a column Superose 12 (Pharmacia Biotech Corp., 1 cm × 30 cm) at UV 206 nm (LKB 2238, SIIBROMMA Corp.). The sample was filtered by 0.45 μm polypropylene filter and diluted to 5 mg/mL in phosphate buffer (NaH$_2$PO$_4$ 0.01 mol/L and Na$_2$HPO$_4$ 0.03 mol/L, pH 7). The degassed phosphate buffer was used as mobile phase at flow of 0.4 mL/min. The column was calibrated by dextran standard sample, which was obtained from Pharmacia Biotech Corp.

Interior morphology observation

The morphology of degraded of PASP hydrogel was observed by scanning electron microscope (SEM) (Hitachi S-4700). The cryofixation technology was applied to observe the swollen hydrogel interstructure. Briefly, the sample was washed by deionized water, and then the water on surface was removed. Then the sample was immediately put into the liquid nitrogen to maintain its swollen state. Subsequently, the sample was freeze-dried for 48 h at −45°C. Finally, the dry sample was taken out, and the surface was coated with gold for SEM observation.

RESULTS AND DISCUSSION

The maintenance of sand crust mechanical strength was critical for the material field application. So the method to enhance mechanical strength and prolong degradation time was major focus of this study. The measurements by controlling crosslinking density and adding composites were proposed.

### Mechanical strength of sand sample with different crosslinking density

Crosslinks provide hydrogel unique properties such as swelling, rigidity, and gradual release of small molecules. By changing the concentration of crosslinking agent, hydrogel could be modulated to meet different applications. The PASP hydrogel synthesized by different concentration of 1,6-hexamethylene diamine (HD) from 0.025 to 0.0375 mol/L was shown in Table II. The PASP was crosslinked by

TABLE II
Characteristics of PASP Hydrogels Crosslinked with Different Concentration of HD

HD (mol/L)	Q_m	Q	M_c (mol/cm^3)
0.0250	284	343	0.406
0.0275	311	375	0.418
0.0300	357	431	0.437
0.0325	382	461	0.447
0.0350	361	435	0.439
0.0375	346	417	0.433

HD, a bifunctional crosslinker, to form three dimensional networks. As the HD concentration increased from 0.025 mol/L, the interchain crosslinks increased with the resulting formation of stable hydrogel that demonstrated by an increase in the swelling ratio. At 0.0325 mol/L of HD, the number of amino and carboxyl group was nearly equivalent, so the crosslinking density (M_c) attained the maximum. When the concentration of HD exceeded 0.0325 mol/L, however, the efficiency of crosslinking decreased as the presence of excessive crosslinking molecules which induced intrachain crosslinks and/or dangling single-end linkage.[11] One would expect that increasing the crosslinking agent, which increases the crosslinking density, would lead to a reduction in swelling ratio. Indeed, Lee et al.[11] and Barbucci et al.[12] found that increasing crosslinking density led to swelling ratio decreased. However, in the current study, swelling ratio showed two distinct regimes: an initial small increase, and then a small decrease after the HD concentration exceeded a certain value. One of main factors that determining the swelling ratio was the hydrogel network size, too big or small size could not contain enough solvent molecules. Initially, when the concentration of crosslinking agent was low, the network size was too big to hold more water molecules. As the concentration of crosslinking agent exceeded a certain value, the network size became too small, the rate of water molecules enter into the networks was slower than the rate of came out, so the swelling ratio reduced gradually. This phenomenon was also observed in our earlier study.[10]

The sample treated by sand fixing agent with different M_c was applied to measure the sand fixing ability (Fig. 2). It could be seen that the sample mechanical strength showed the same change tendency: the compressive strength increased from 0.723 to 0.981 MPa, and then the value decreased to 0.832 MPa when the concentration of crosslinking agent increased further. This could be explained that as crosslinking density increased, the three-dimensional network formed gradually and the electrostatic interactions (Coulombic and van der Waals) between groups on the chain increased, so the interaction
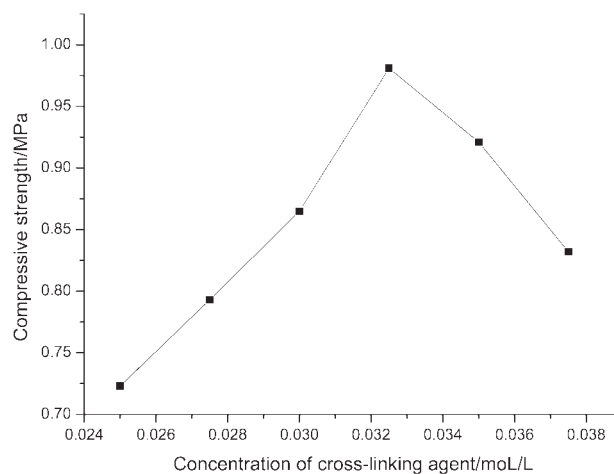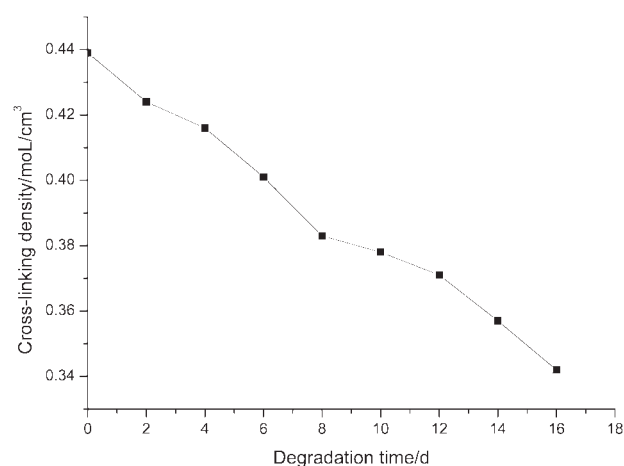

Figure 2 The relation between the concentration of HD and compressive strength.

force between the sand fixing agent and sand particle increased. However with the molecular weight of chains between two successive crosslinks decreased, the interaction between groups decreased, and the sand fixing ability decreased consequently.

Degradation time and sand fixing property

It is well known that polymer degrades through chemical, physical, and microbial mechanisms, whereas the microbial degradation via break of crosslinks was the focus of this study. The change of crosslinking density of PASP during degradation process was measured (Fig. 3) and it showed that the crosslinking density decreased continuously with degradation time increasing. The Figures 4 and 5 showed the relation between sand fixing properties and degradation time. It appeared that the compressive

Figure 3 The relation between the degradation time and crosslinking density at HD concentration of 0.035 mol/L.
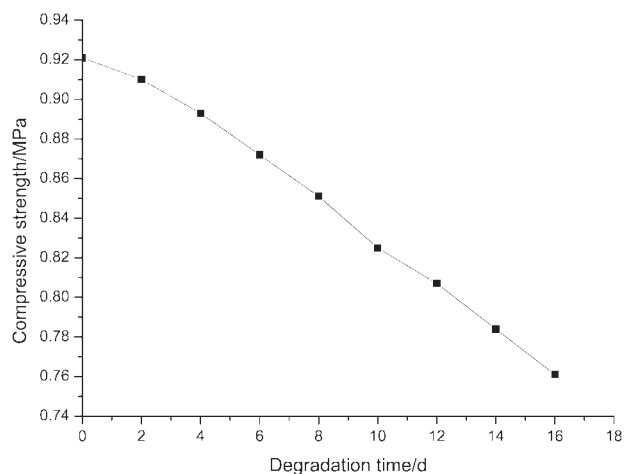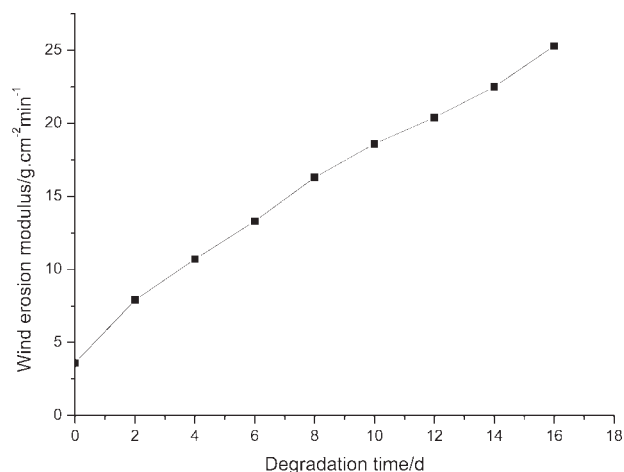
Figure 4 The relation between the degradation time and compressive strength at HD concentration of 0.035 mol/L.

strength decreased and wind erosion modulus increased with increasing degradation time.
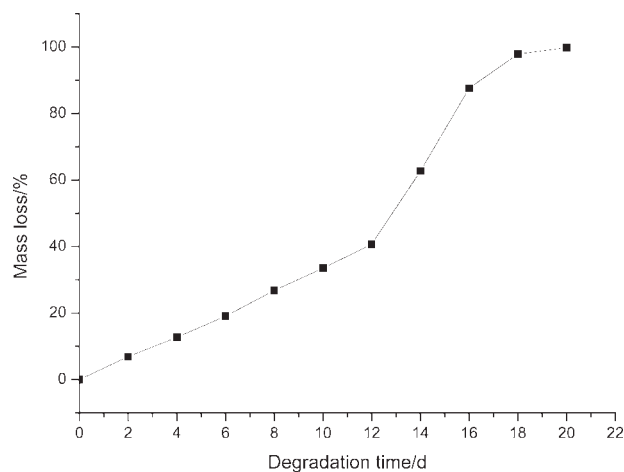
Degradation time and mass loss

The physical and mechanical behaviors of the material were heavily relied on the backbone chemistry of the polymer and the crosslinking density of the network. As degradation occurred, the ester linkages between HD and PASP broke homogeneously throughout the degradation process. This ongoing break of crosslinks within the polymer decreased the crosslinking density of the network. Therefore, the microscopic break of the network led to the bulk erosion of the sample over the time and eventual macroscopic broke down of the structure.

The mass loss of PASP was shown in Figure 6 and it occurred after the sample was placed in the soil. The curve initially appeared linear one, corresponding to an approximately constant mass loss rate.

Figure 5 The relation between the degradation time and wind erosion modulus at HD concentration of 0.035 mol/L.

Figure 6 The relation between the degradation time and mass loss of hydrogels in soil at HD concentration of 0.035 mol/L.

While during the last 60% of mass loss, the slope of the curve increased and almost instantaneous loss of the remaining product was observed. This increase rate of mass loss during the final stage of degradation could be attributed to higher molecular weight erosion segments released from the bulk chain. For example, during the later stage of degradation, the probability of releasing degradation segments which composing several backbones of PASP became significantly. It can be seen that the PASP mass loss attained to 99.8% at 20 days, whereas the earlier study found it needed 9 days to attain the maximal strength.[13] Therefore, the PASP met the requirement that it degraded after the crust formed.

SEM observation

The interior morphological changes of PASP hydrogel were shown in Figure 7. As the degradation proceeded, the network size became large and edge of pore was found irregular. This was in agreement with the result discussed in the mass loss section.

Degradation behavior of PASP composites

To improve the PASP sand fixing property and prolong degradation time, some biodegradable composites were added (Table III). The effect of composites on degradation behavior and sand fixing property were shown in Figure 8. It showed that the introduction of composites could retard degradation process and provide better sand fixing property. The primary structure of xanthan gum includes cellulosic backbone (β-D-glucose residues) and a trisaccharide side chain of β-D-mannose-β-D-glucuronic acid-α-D-mannose attached with alternate glucose residues of
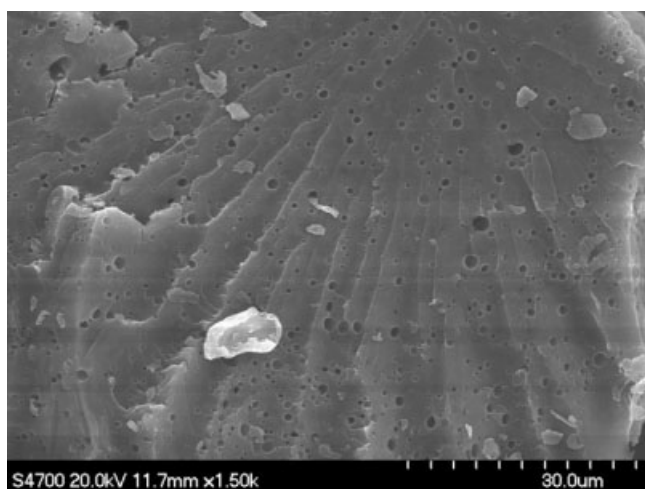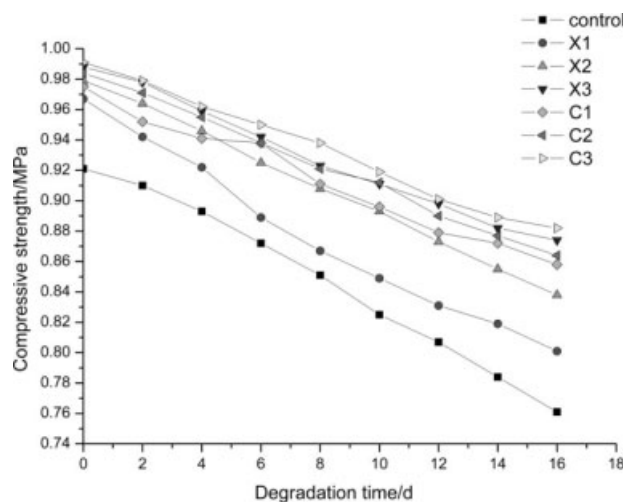
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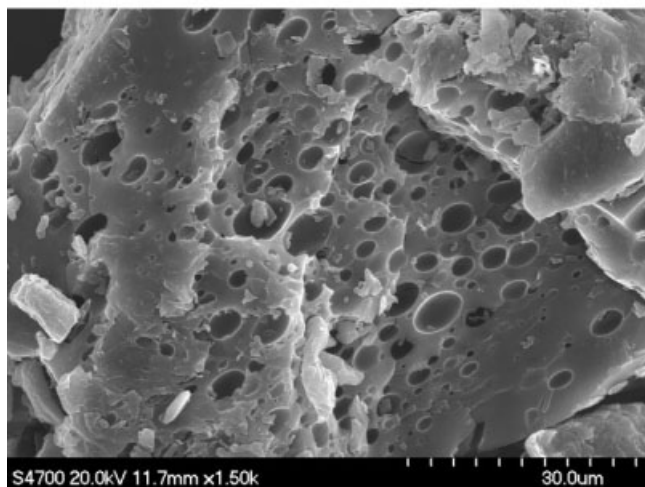
(b)

Figure 7 SEM images of degraded PASP hydrogel in soil at HD concentration of 0.035 mol/L: (a) 4 days and (b) 10 days.

main chain, whereas anionic linear carrageenan consists of alternating α-1,4 and β-1,3 linked anhydrogalactose residues, these polysaccharides' unique structure make they were stable in the presence of enzyme. Therefore, the addition of xanthan gum and κ-carrageenan increased the stability in the degradation process.

TABLE III
The Degradation Time of PASP Composites

Composite category	Sample code	Molar ratio of composite and PASP	Full degradation time/d
xanthan gum	X1	1 : 1	21
	X2	2 : 1	23
	X3	3 : 1	25
κ-carrageenan	C1	1 : 1	23
	C2	2 : 1	25
	C3	3 : 1	27

Figure 8 The relation between the degradation time and compressive strength of PASP composites (HD concentration of 0.035 mol/L).

Mechanism of degradation

Because of the low water content in soil, it could be recognized that the degradation of PASP hydrogel through the microbial mechanism via break of crosslinks. The molecular weight change for PASP degraded in the soil was shown in Figure 9. It was shown that the degradation process was fast initially and then became slowly at subsequent time. The degradation initially occurred on the crosslinkages, which played the role to connect the polymer chains and formed the three-dimensional networks, so the molecule decreased fast. In addition, due to the scission of crosslinkage, the backbone of polymer could not maintain the long-range connectivity, so the degradation of networks significantly increased chain mobility, and the crosslinking density reduced fast
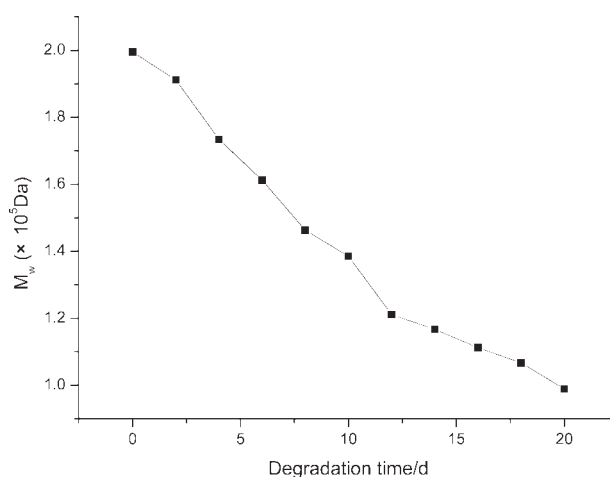
Figure 9 The relation between the degradation time and molecular weight of PASP at HD concentration of 0.035 mol/L.

initially. Finally, with the disappearance of three-dimensional networks, the polymer became totally water soluble and the mass loss reduced at an accelerative rate.

CONCLUSIONS

The crosslinking density of PASP with different concentration of HD was calculated by Flory-Rehner equation. The mechanical strength of crust relied on the sand fixing agent crosslinking density, and it was found the crust compressive strength attained the maximum when the polymer crosslinking density was 0.447 mol/cm^3. The sand fixing agent crosslinking density, molecular weight, and sand fixing properties decreased with degradation increasing. The PASP degraded after the crust attained the maximal strength and the PASP composites could increase sand fixing property and prolong degradation time when compared with the control.

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