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Synthesis and characterization of a novel soil stabilizer based on biodegradable poly(aspartic acid) hydrogel

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Abstract−A novel soil stabilizer based on poly-amino acid - polyaspartic acid (PASP) and its copolymer which modified by xanthan gum (XG) was studied to increase soil particle compressive strength and resistance to wind erosion. Due to its unique property, the stabilizer aggregated individual soil particles and formed crust. The sample compressive strength increased from 0.175 to 0.612 MPa and the wind erosion modulus reduced from 22.43 to 10.56 $g \cdot m^{-2} \cdot min^{-1}$ after the 1% PASP hydrogel was applied by 1.67 Lm^{-2} (1 cm of crust). The soil water content was higher than the control due to the polymer's excellent water-retaining property. The polymer had no negative influence on seed germination and growth. The biodegradability experiment showed that PASP was easy to biodegrade and therefore it was safe to apply in the field.

Key words: Wind Erosion, Soil Stabilizer, Compressive Strength, Poly(aspartic acid), Xanthan Gum

INTRODUCTION

Wind erosion is one of the most serious environmental pollution problems and it is a complex process due to many factors involved [1,2]. It could cause much damage such as crop decrease, soil fertility reduction, dust storms and land degradation [3-5]. Many methods, including planting trees, erecting hedges and mulching crop residue, have been carried out to reduce the damage [6,7]. However, these methods have some problems such as being time and labor consuming, with low effectiveness and high cost.

Hydrogels are a kind of three-dimensional cross-linked hydrophilic polymers, which can adsorb hundreds of times of water of their own weight [8-11]. The biocompatibility and biodegradation of poly(amino acid) make them ideal candidates for many applications in detergents, cosmetics, biomedicines and horticultural fertilizers. Poly(aspartic acid) (PASP) belongs to the family of chemical synthetic poly(amino acid) with free carboxylic groups on chain and it is synthesized by thermal polycondensation of aspartic acid (ASP) and ammonium salts of maleic acid to form polysuccinimide (PSI) [12]. The high molecular weight polymer is widely used as scale inhibitor, corrosion inhibitor, pesticide, fertilizer and superabsorbent material [13,14]. Xanthan gum (XG) is a natural polysaccharide and an important industrial biopolymer. The high molecular weight polysaccharide has been extensively studied because of its property that would allow it to be used as a supplement for other natural and synthetic water-soluble gums [15].

The polymer studied in this paper was applied as soil stabilizer to increase sample compressive strength and resistance to wind erosion. The relation between the soil physical properties (including water content, wind erosion modulus and compressive strength) and the different application conditions (including the thickness of crust, time to reach the maximum strength and repeat hydration-dehydration cycles) was determined. The fundamental method to control wind erosion is to combine with biotechnology methods that help soil restore its original physical properties. All kinds of artificial methods provide a relatively suitable environment for seeds and plants to germinate and grow. Once a plant can grow in a field, its roots could aggregate the surrounding soil particle and finally solve the problem. Therefore, the seed germination experiment was designed to evaluate whether the polymer had negative influence on vegetation growth. In addition, the PASP biodegradability, including the biological oxygen demand (BOD), chemical oxygen demand (COD) and field degradation was measured, respectively.

MATERIALS AND METHODS

1. Materials

L-aspartic acid was obtained from Beijing chemical reagent company. N,N-Dimethylformamide (DMF) and 1,6-hexamethylene diamine (HD) were used without any further purification. The concentration of sodium hydroxide solution was adjusted to 27% (wt%).

2. Preparation of PSI and PASP with High Molecular Weight

L-Aspartic acid (5 kg) and 85% phosphoric acid (2.146 kg) 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. Then the product was washed with water until neutral and then dried at 85 °C under a vacuum of 0.09 MPa. Finally, a yellowish powder of PSI was obtained.

The hydrolysis of PSI was performed in an ice bath by adding 2 g of PSI, 1.5 g sodium hydroxide and 10 ml deionized water into a 100 ml beaker with a magnetic stirring bar. After the hydrolytic reaction for 1 h, the pH of the solution was adjusted to neutral by adding 35% HCl solution. Then, 70 ml methanol which was saturated with sodium chloride was poured into the beaker, and the precipitate was recovered by a filtration and dried at 40 °C under a vacuum condition (Fig. 1).

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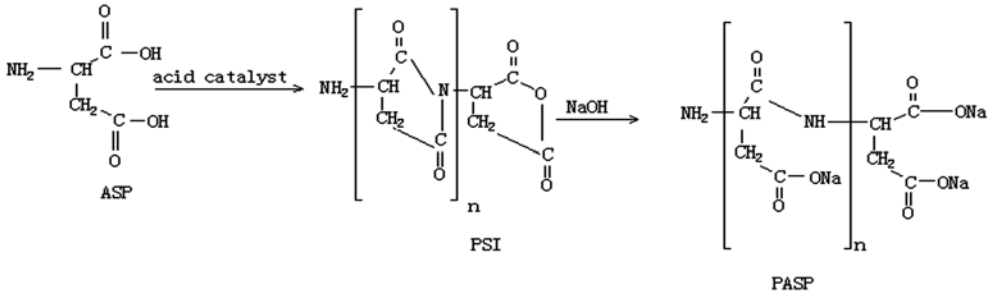

Fig. 1. Preparation of PSI and PASP.

3. Preparation of Cross-linked PASP Hydrogels and its Composites

PASP resin was prepared from PSI, which was synthesized by thermal polycondensation of L-aspartic acid. One gram PSI was dissolved in 28 ml DMF in a 250 ml beaker with 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 0.07 g 1,6-hexamethylene diamine used as cross-linking agent was added into the beaker. The cross-linking reaction was carried out for 1 h at 40 °C. After the cross-linked polymer had formed, the imide rings of the cross-linked polymer were hydrolyzed with 27% NaOH at 40 °C until pH was 9. Then 100 ml ethanol was added and the precipitate was dried by vacuum drying at 40 °C. Thereby, the cross-linked PASP was obtained. For PASP composites synthesis, the composites were added to the reactor with cross-linking agent and the following process was the same as above.

4. Grain Size of Soil

The soil sample was collected from Beijing University of Chemical Technology campus. The grain size analysis of the soil used for this study is presented in Table 1. The dominant component of the soil was a particle size between 0.55-0.35 mm.

5. Sample Property Test

5-1. Compressive Strength Test

The sample for the strength and wind erosion test was prepared by the following process: a certain amount of resin was added into tap water to prepare hydrogel at room temperature and the hydrogel was sprayed over the soil which was in a rectangular aluminum container (35×45 cm, 4 cm depth). The container was placed in an oven at 60 °C for 24 h and then the crust was formed. The strength of crust was measured on the press machine (W-100, 0-2 MPa with a resolution of 0.001 MPa) that was purchased from the Beijing JianQiang Instrument Company, China. The strength was loaded on the central part of crust until cracks appeared. To ensure no systematic effect due to position within the container, the strength was measured at four locations on each crust surface at randomly and their average values were recorded.

5-2. Wind Erosion Test

The wind erosion of the crust was measured by a portable wind tunnel. It was a low-speed, straight closed-throat wind tunnel. An axial fan with 6 blades which could provide a wind speed from 2-16 $m \cdot s^{-1}$ was mounted at the front of the wind tunnel. The portable wind tunnel had a length of 1.2 m, with a cross-section of working section having a diameter of 0.12 m, and 0.5 m long. Before the test, a soil sample (6 cm in width, 8 cm in length and 3 cm in height with a known weight) was placed on a flat that was under 1 cm from the central line of tunnel and 90 cm from the fan. The weight of soil loss during each wind tunnel test was calculated by comparing the weight difference before and after the test, and the weight loss in grams was converted to erosion modulus ($g \cdot m^{-2} \cdot min^{-1}$).

5-3. Effect of Repeat Hydration-dehydration Cycles

A hydration-dehydration cycle test was performed as follows: a certain amount of 1% PASP hydrogels (1.67 Lm^{-2}) was sprinkled over the surface of soil evenly and it was placed in the oven at 60 °C for 24 h. Then the strength and wind erosion modulus properties were measured. This corresponded to the "first" cycle and there were 15 cycles involved in the test.

6. Seed Germination Experiment

The seed germination test was designed to study the influence of polymer on seed germination. The soil water content was adjusted to 10% and it was placed in a rectangular plot (30×35 cm). 45 *Astragalus adsurgen* seeds were pressed into the soil (2 cm in depth) by fingers and then the hydrogel (1%PASP, 1.67 Lm^{-2}) was sprinkled evenly on the soil surface. The seeds were germinated in a well ventilated and non-heated room at ambient temperature and natural indirect light; the air temperature and relative air humidity were maintained at 25 °C and 35%, respectively. The criterion for germination was the emergence of the radicle and germinated seeds were removed. The germination rate was expressed as percentage of viable seeds germinated:

germination rate (%)
=number of germinated seeds/number of seeds initiated×100

Table 1. Grain size of experimented soil (in weight percent)

Grain size distribution (mm)					
>1.05	1.05-0.80	0.80-0.55	0.55-0.35	0.35-0.15	<0.15
8.45±1.13	12.01±1.64	10.92±1.54	41.4±5.78	10.72±1.08	16.5±1.48

(mean±SD; n=4)

7. Water-retaining property

The PASP and its copolymer have excellent water-absorbent property, so the following experiment was designed to evaluate the water-retaining capacity when they were applied in soil: 250 g soil that mixed with polymer was filled in plastic container (12 cm in diameter, 6 cm in depth). Then 100 g tap water was added and the container was placed on tables in an air temperature constant room (25 °C, air relative humid 20%). The soil water content was determined by taking a small sample from the surface every 24 h, oven-drying at 105 °C for 24 h and determining weight loss:

water content (%)
=(wet soil weight−dry soil weight)/wet soil weight×100

8. Biodegradability of PASP and its Composites

The BOD and COD of PASP and its copolymer were measured according to Japanese Industrial Standards (JIS) K6950 [16]. The biodegradability of a material is evaluated by the value of BOD/COD: if the value of BOD/COD is larger than 0.45, it means the material can be easily biodegraded. If the value is larger than 0.3, it means the material can be biodegraded or it cannot be biodegraded easily, and if the value is lower than 0.25, it means the material is hard to be biodegraded. In addition, a field experiment was also carried out: the weighted soil stabilizer was enclosed in a 250 mesh tea-bag and buried in soil (25 cm in depth at Beijing University of Chemical Technology campus). At regular time intervals, the weight loss was determined. The degradation time was defined as the time needed to full degradation (W_t=0) and the degree of degradation was calculated by following equation:

$$\text{masslost}\% = \frac{W_i - W_t}{W_i}$$

where W_i and W_t are the initial and at specified time weight of sample during degradation process after drying in a vacuum oven, respectively.

RESULTS AND DISCUSSION

1. Effect of Crust Thickness

It could be expected that the soil compressive strength and wind erosion modulus significantly depended on the thickness of crust. As the crust thickness increased, the sample compressive strength increased and wind erosion modulus decreased distinctly (Table 2, Fig. 2). When the crust thickness increased from 0.5 to 3 cm, the compressive strength increased from 0.303 to 1.132 MPa in the case of 0.5% PASP hydrogels. This could be explained by the fact that

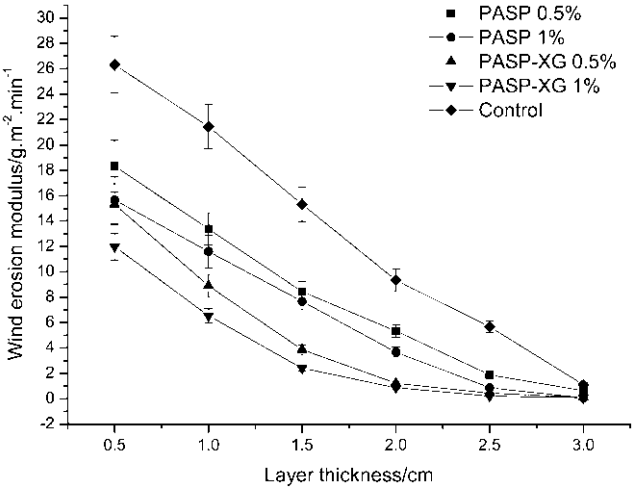

Fig. 2. The relationship between wind erosion modulus and sample thickness under different concentrations at application of 1.67 Lm^{-2} and the wind velocity of 8 m·s^{-1} from the wind tunnel experiment (mean±SD; n=4).

PASP is a negative polymer. When it swells in water and mixes with soil, it aggregates soil particles through charge attraction: complex electrostatic interaction occurs and the soil compressive strength increases. In addition, there was also a marked difference between PASP and PASP-XG: PASP-XG could further improve compressive strength at the same concentration compared to PASP: when the crust thickness was 2 cm, the compressive strength of sample reached 1.058 MPa in the case of 0.5% PASP-XG solution, whereas that value was 0.982 MPa in the case of PASP solution. The primary structure of XG includes cellulosic backbone (β-D-glucose residues), and a trisaccharide side chain of β-D-mannose-β-D-glucuronic acid-α-D-mannose attaches with alternate glucose residues of the main chain. So the anionic character of this polymer is due to the presence of both glucuronic acid and pyruvic acid groups on the side chain. When XG is incorporated with PASP, it could increase electrostatic interaction and aggregate soil particles tighter.

2. Effect of Hydration-dehydration Cycles

The maintenance of the crust strength durability is very important when the polymer is applied in an arid region. The PASP and its copolymers are hydrophilic polymers, so if the material is subjected to repeat hydration-dehydration cycles, it may lose mechanical strength and decrease the soil stabilizing property. While in an arid area where rainfall events may be frequent but small, the crust is likely to become partially imbibed, or undergo periodic hydration

Table 2. The relationship between compressive strength and crust thickness under different concentrations at application of 1.67 Lm^{-2}

Compressive strength (MPa)		Crust thickness (cm)					
		0.5	1	1.5	2	2.5	3
PASP	0.5%	0.303±0.041	0.474±0.049	0.726±0.106	0.982±0.111	0.997±0.153	1.132±0.144
	1%	0.484±0.051	0.612±0.065	0.881±0.071	1.185±0.108	1.237±0.118	1.344±0.127
PASP-XG	0.5%	0.405±0.049	0.522±0.042	0.771±0.062	1.058±0.097	1.133±0.095	1.245±0.119
	1%	0.579±0.041	0.727±0.085	0.976±0.101	1.258±0.129	1.372±0.127	1.482±0.167
Control		0.104±0.011	0.175±0.014	0.229±0.028	0.313±0.033	0.395±0.034	0.437±0.045

(mean±SD; n=4)

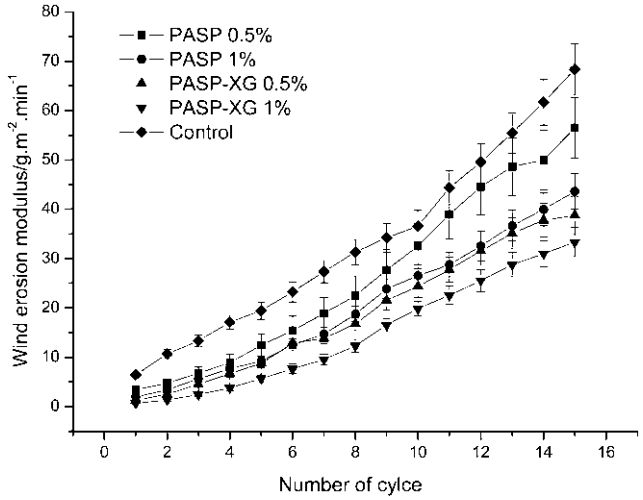

Fig. 3. Influence of hydration-dehydration cycles on sample wind erosion modulus at application of solution of 1.67 Lm^{-2} and the wind velocity of 12 $m \cdot s^{-1}$ from the wind tunnel experiment (mean±SD; n=4).

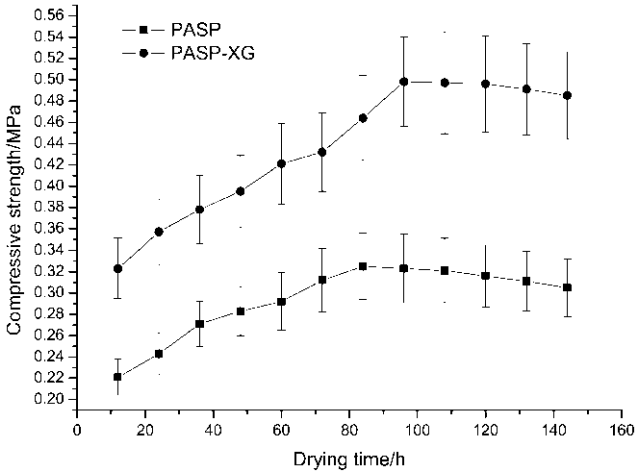

Fig. 4. The relationship between drying time and sample compressive strength at the crust thickness of 2 cm and the concentration of solution of 0.5% at 1.67 Lm^{-2} (mean±SD; n=4).

and subsequently dehydration. It could be seen that the compressive strength and wind erosion modulus relied heavily on hydration-dehydration cycles (Fig. 3, Table 3). The strength of crust decreased with the cycles increasing: the compressive strength decreased from 0.97 to 0.802 MPa in case of 0.5% PASP hydrogels, from 1.155 to 0.893 MPa in case of 1% PASP-XG solution, respectively. A corresponding trend could be found in the wind erosion experiment. During the cycles, the polymer subjected to hydration and dehydration cycles, the electrostatic interactions between polymer and soil particles decreased, so the compressive strength of crust decreased. After 13 cycles, some visible cracks appeared on the surface of the sample, so hydration-dehydration was a crucial factor affecting the durability of the mechanical property of the polymer.

3. Time to Maximum Strength (T_{max})

In order to study the time of crust to reach the maximal mechanical strength when the sample dried in the oven at 60 °C, the sample was taken out every 12 h. The result showed the compressive strength was different during the drying process (Fig. 4). The T_{max} for PASP and PASP-XG was 84 and 96 h, respectively. During the drying process, water evaporated from soil and the strength reached a maximum gradually, then the strength declined slight. At an early stage (before T_{max}), the water in the soil did not evaporate completely, so the value was lower than the maximum. When the drying process continued, the weight of soil became constant and the poly-

Table 3. Influence of the number of hydration-dehydration cycles on sample compressive strength at application of 1.67 Lm^{-2} and crust thickness of 2 cm

Cycle number	Compressive strength (MPa)				
	PASP 0.5%	PASP-XG 0.5%	PASP 1%	PASP-XG 1%	Control
0	0.970±0.121	1.000±0.132	1.022±0.145	1.155±0.187	0.323±0.034
1	0.958±0.119	0.987±0.132	0.996±0.126	1.113±0.193	0.319±0.045
2	0.951±0.114	0.984±0.128	0.990±0.130	1.107±0.153	0.314±0.027
3	0.948±0.113	0.975±0.128	0.984±0.137	1.090±0.128	0.310±0.026
4	0.925±0.105	0.969±0.134	0.979±0.145	1.007±0.163	0.305±0.025
5	0.920±0.101	0.966±0.109	0.975±0.130	0.989±0.147	0.301±0.029
6	0.914±0.118	0.958±0.114	0.965±0.110	0.981±0.131	0.297±0.017
7	0.905±0.117	0.948±0.108	0.959±0.121	0.969±0.104	0.292±0.032
8	0.889±0.105	0.940±0.108	0.946±0.111	0.957±0.126	0.288±0.024
9	0.874±0.108	0.930±0.118	0.940±0.111	0.951±0.136	0.282±0.019
10	0.861±0.102	0.922±0.113	0.936±0.117	0.945±0.112	0.278±0.021
11	0.844±0.112	0.904±0.121	0.926±0.133	0.940±0.139	0.273±0.011
12	0.834±0.087	0.885±0.098	0.911±0.083	0.937±0.101	0.268±0.027
13	0.822±0.090	0.878±0.081	0.903±0.072	0.927±0.089	0.264±0.029
14	0.819±0.097	0.854±0.092	0.888±0.098	0.910±0.107	0.261±0.020
15	0.802±0.077	0.837±0.083	0.874±0.103	0.893±0.108	0.256±0.023

(mean±SD; n=4)

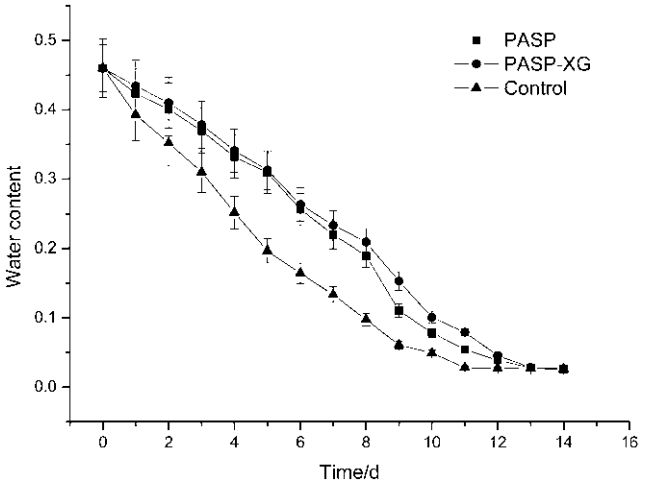

Fig. 5. The relationship between the soil water content and evaporating time under 20 °C and 30% relative humidity (mean± SD; n=4).

Table 4. Influence of crust on seed growth at polymer application of 1.67 Lm^{-2}

Polymer	Layer thickness (cm)	Germination rate (%)
PASP (0.5%)	0.5	83.2±8.4(86.3±8.7*)
	1.0	82.5±8.3
	1.5	81.8±8.3
	2.0	80.8±8.2
	2.5	78.3±7.8
	3.0	75.1±7.7
PASP-XG (0.5%)	0.5	84.1±8.5
	1.0	83.5±8.5
	1.5	81.3±8.2
	2.0	80.6±8.0
	2.5	78.3±7.6
	3.0	74.7±7.3

*Value of control (seed germination in soil unmodified by polymer), (mean±SD; n=4)

mer aging effect dominated the changes, so the value declined slightly.

4. Water-retaining Capacity

PASP hydrogels have excellent water-absorption, water-retaining and anti-evaporation properties. Fig. 5 demonstrates the result of soil water content treated with polymer (0.5%, based on soil weight) and it can be seen that the soil water content was evidently higher than that of the control during 14 days. However, there was no significant difference between PASP and PASP-XG in the first 6 days. A possible reason may be that the soil water content was relatively high initially, so the resin water absorbent capacity was not fully utilized. After 6 days, the free water in soil almost evaporated, and the water absorbed by resin began to evaporate, so there was relatively a significant difference between PASP and PASP-XG.

The effect of water-retaining capacity on natural plant populations is likely to be important. In the field, relatively hard water availability occurs during drought seasons and the rainfall events in desert zones are highly unpredictable. It is important for plants holding water when rainfall occurs and survive during drought time. Therefore. the PASP resin could absorb water when rainfall occurs and release water gradually.

5. Polymer Influence on Seed Growth

When plants need to grow on sand or sandy soil, the seed should be protected from wind erosion and it can grow through the crust easily. According to Table 4, the seed germinated and grew in the soil treated with polymer without significant influence. So the material may be suitable to reduce wind erosion with plant method.

6. Environment Evaluation and Economic Assessment

To study the biodegradability of PASP and its composites, the values of BOD and COD were measured (Table 5). The values of BOD/COD were bigger than 0.45, which meant the PASP and its copolymers were environment friendly products and therefore were safe to apply in fields. The physical and mechanical behavior of the material heavily relies on the backbone chemistry of the polymer and the cross-linking density of the network. As degradation occurred, the ester linkages between cross-linking agent and PASP broke homogeneously throughout the entire process. This ongoing break of cross-links within the polymer decreased the cross-linking density of the network. Therefore, the microscopic break of network of the network led to the bulk erosion of the sample over time and eventual macroscopic breakdown of the structure. According to field degradation experiment, the PASP and PASP-XG totally degraded within 28 days (Fig. 6). In addition, it was estimated that the final product of PASP was 1,800 ton^{-1} and the application cost was about 0.025 m^{-2} at 1.67 Lm^{-2} at concentration of 1%.

CONCLUSIONS

PASP could significantly increase soil compressive strength and resistance to wind erosion. The compressive strength of sample decreased with the cycle of hydration-dehydration increasing. The compressive strength reached the maximum within 84-96 h. The water-retaining property of polymer could decrease water evaporation and benefit seed germination and growth in an arid environment. The polymer had no negative influence on the seed germination and growth, so it is suitable to control wind erosion with vegetative method. The BOD, COD and field degradation experiment indi-

Table 5. Biodegradability of PASP and its composites

Sample	Biodegradation degree (%) from BOD data	Biodegradation degree (%) from COD data	Biodegradability from BOD/COD data
PASP	25.9±2.3	73.5±8.3	0.561±0.066
PASP-XG	22.4±2.1	67.3±6.5	0.538±0.068

(mean±SD; n=4)

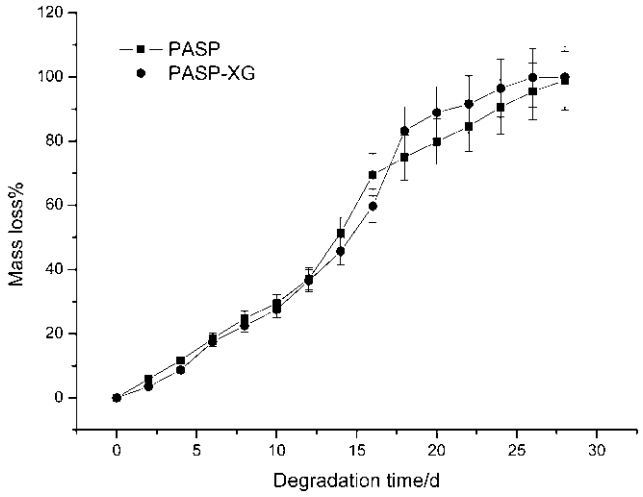

Fig. 6. The relation between the degradation time and mass loss of PASP and PASP-XG in soil (mean±SD; n=4).

cated that the PASP and its copolymer were biodegradable.

ACKNOWLEDGMENTS

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