

Short Communication

Preparation and Property of Poly (acrylamide-co-acrylic acid) Macromolecule Slow-releasing Fertilizer

Wanjie Li, Liqin Zhang, Chengcen Liu, Zhenhai Liang*

College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, P.R China

*E-mail: liangzhenhai@tyut.edu.cn; liangzhenh@sina.com

Received: 29 September 2012 / Accepted: 19 October 2012 / Published: 1 November 2012

The aim of the study was to prepare a poly (acrylamide-co-acrylic acid) macromolecule slow-releasing fertilizer (PMSF) by electrochemistry method. The acrylamide, acrylic acid and Urea were polymerized and grafted on the Ti/PbO₂ electrode by adding the cerium (Ce(IV)) as initiator. Then after drying and smashing, the PMSF was obtained. The PMSF was characterized by infrared spectroscopy (IR) and thermo gravimetric Analysis (TG). The influence on concentrations of Urea and KH₂PO₄ were discussed. The contents of nitrogen, phosphorus and potassium in the PMSF were determined by the spectrophotometer. By simulating the process of release, the release mechanism of PMSF was obtained. The results showed that a new macromolecule slow release fertilizer which contains nitrogen, phosphorus and potassium can be prepared by electrochemical method. Both the IR and TG proved the existing of Urea in PMSF. The form of phosphorus and potassium in the MSRF existed by ions. The best technological parameters of the process were obtained: $\omega(\text{AM})=9\%$, $\omega(\text{AA})=4.1\%$, $\omega(\text{Ce(IV)})=1\%$, $I=0.05$, $\omega(\text{Urea})=7.2\%$, $\omega(\text{KH}_2\text{PO}_4)=5.4\%$. The total contents of the nitrogen, phosphorus and potassium in the PMSF can achieve a content of 58.5%. Among which, nitrogen 32.5%, phosphorus 13%, potassium 13%. The effective components can release 80% within 60 days.

Keywords: Electrochemistry; Macromolecule; slow-release fertilizer

1. INTRODUCTION

Fertilizer and water are important factors that limit the production of agriculture. So it is very important to improve the utilization of water resources and fertilizer nutrients [1]. One possible way to improve nutrients use efficiency while reducing the environmental hazards is by using slow-release fertilizers. Compared to the conventional type, slow-releasing fertilizers have many advantages, Such

as decreasing fertilizer loss rate, supplying nutrients sustainably, lowering application frequency and minimizing potential negative effects associated with overdosage [2,3].

Slow-releasing fertilizers have long been recognized as the best solution to the various environmental problems caused by traditional water-soluble fertilizers. With slow-release fertilizers, dosage requirements are lowered, fertilizer use efficiency is improved and environmental pollution problems are practically negligible. Slow-release fertilizers are of various types depending on the mechanisms of slow-release. [4, 5]

Slow-releasing fertilizers have been made by many methods, such as coating[4], mixing metal ion[6] and so on. Basu[7] has made a slow-releasing fertilizer with the method of coating from polyacrylamid But these methods have many drawbacks, such as environmental pollution, with side reaction, releasing incompletely and so on. The electrochemical method has the advantages of cleaning, activity and environment friendly.

2. EXPERIMENTAL

2.1 Materials

Acrylamide (AM, chemical grade), Acrylic acid (AA, chemical grade, Beijing Eastern Chemical Works, Beijing, China), Ce (IV), Urea (chemical grade), KH_2PO_4 . Ti/PbO₂ electrode.

2.2 Preparation of slow-releasing fertilizer

9g of AM and 4.1 mL AA were first dissolved in a small amount of distilled water. Then the H_2SO_4 (0.5mol/L) were added as the electrolyte. The initiator was Ce (IV). Then provide the power to polymerize at the atmosphere of nitrogen. The Urea was added to the system after 3 hours. The KH_2PO_4 was mixed at the end of the polymerization. Then cease the power and precipitate the polymer by ethanol. After drying, and smashing, the MSRF was obtained.

2.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out with Nicolet NEXUS 670 FTIR spectrometer. The samples were dried completely and ground to fine power, then pushed down to piece blending with KBr.

2.4. Determination of effective content

The nitrogen and phosphorus contents of MSRF were determined by the spectrophotometer.

2.5 Slow-release behavior of Slow-releasing fertilizer in soil

To study the slow-release behavior of PMSF in soil, the following experiment was carried out: 1 g of Slow-releasing fertilizer was well mixed with 200 g of dry soil and kept in a 200 mL glass beaker properly covered and incubated for different periods at room temperature. Throughout the experiment, the soil sample was maintained at 30 % water-holding capacity by weighting and adding tap water if necessary, periodically. After 5, 10, 15, 20, 25, 30, 40, 50 and 60 days, the remaining granules in the beaker were picked out, washed with distilled water, and then dried at 70°C to a constant weight to be estimated for the content of nitrogen.

3. RESULTS AND DISCUSSION

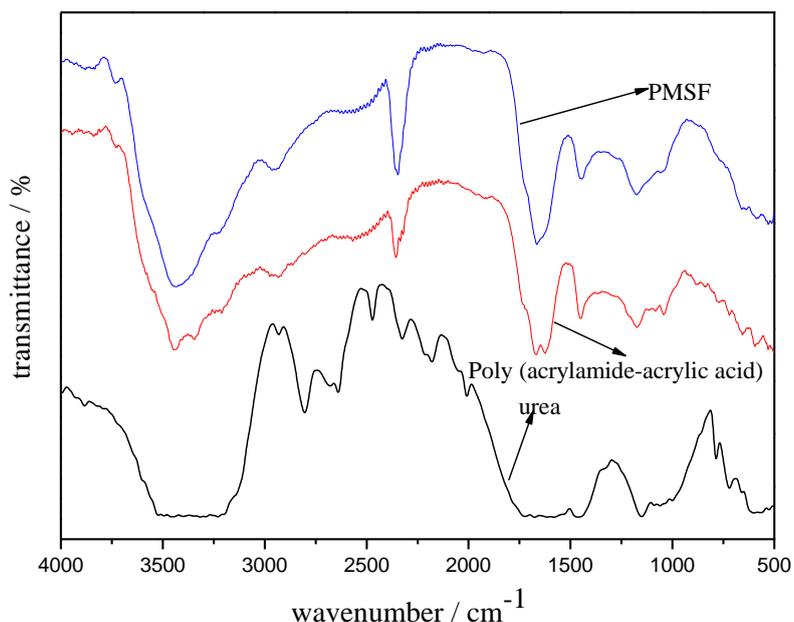


Figure 1. FT-IR spectra of P(AA-co-AM), Urea and PMSF

3.1 FT-IR spectra of the P(AA-co-AM), Urea and PMSF

Fig. 2 shows the FTIR spectra of P(AA-co-AM), Urea and PMSF. The curve of PMSF was much alike to the curve of P(AA-co-AM), which proved the P(AA-co-AM) was the main component of the PMSF. At 1733 cm^{-1} for C=O stretching of acrylate unit in the curve of PMSF. At 2334 cm^{-1} for N-H stretching, this was appeared in all the three lines. And the intensity was strong in the PMSF, which shows that the PMSF was combined by P(AA-co-AM) and Urea. It is noted that, at 1637 cm^{-1} for C=O stretching was acrylamide unit in the PMSF line.

3.2 Thermo gravimetric Analysis (TG)

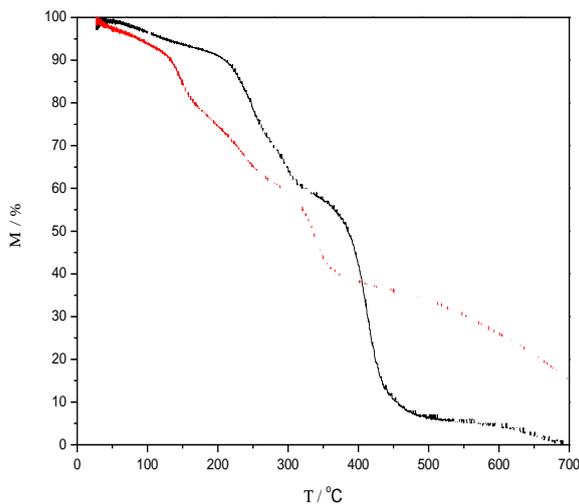


Figure 2. Thermography analysis of Urea and PMSF

Fig. 2 reflects the change of the quality with the temperature. As is shown in the red curve of the figure 2, the decomposition temperature of Urea is 120°C. When the Urea was grafted at the P(AA-co-AM), the decomposition temperature was increased to 200°C. Figure 2 shows that the grafting reaction effects Urea at a certain extent, but the Urea was existed in the fertilizer with the form of small molecule. This chart proved that the method of electrochemistry grafting polymer was success because the fertilizer efficiency of the Urea was no change.

3.3 Influence of the Urea concentration

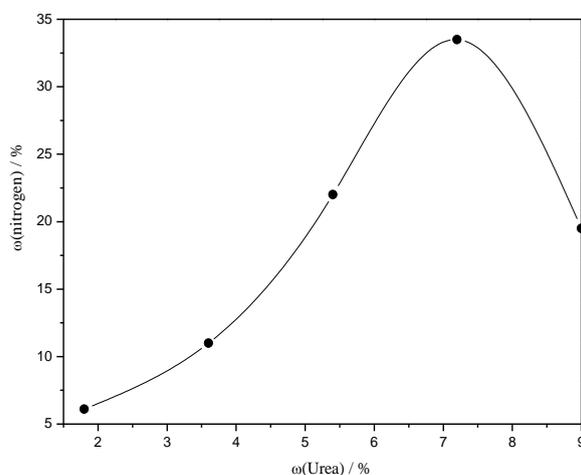


Figure 3. Relationship between the concentration of Urea and the fertilizer efficiency

Fig. 3 shows the Relationship between the concentration of Urea and the fertilizer efficiency of MSRF, the best dosage of the Urea is 7.2g. The content of the Nitrogen in MSRF is increase with the dosage of the Urea at a special range. This line shows the Urea played an important role in the process of the grafting. By using the spectrophotometer we known that the form of the Urea existed in the fertilizer was molecular. This phenomenon shows that the grafting way of Urea was electric charge effecting but not the bond breaking. As is known, there are a large number of charged free radicals in the electrochemical system[10], which offers a possibility for the urea combined by electric charge. The combined way of the urea and poly(AM-co-AA) was hydrogen bond maybe.

3.4 The effect of Phosphorus to the fertilizer

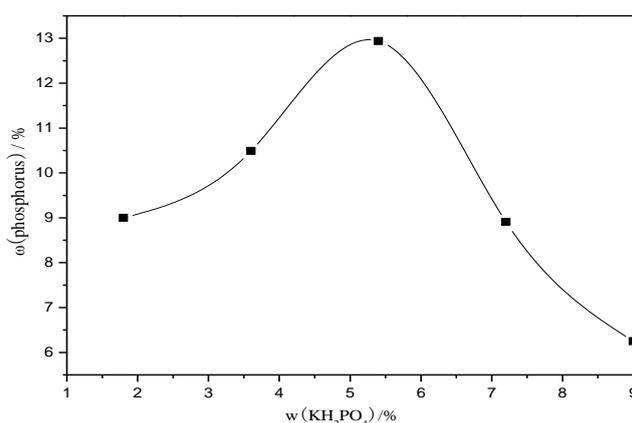


Figure 4. Relationship between the concentration of KH₂PO₄ and the fertilizer efficiency

Fig. 4 shows the Relationship between the concentration of KH₂PO₄ and the fertilizer efficiency, the best dosage of the KH₂PO₄ is 5.4g. The same as Urea, the trend of the effect is parabola. The KH₂PO₄ was mixed to the grafting product. Dissolution equilibrium existed of the KH₂PO₄, so there was a limited for its quantity. The mixed way makes the phosphorus and potassium easy to release into the soil.

3.5 Nitrogen slow-release behavior in soil

Fig. 5 shows the nitrogen slow-release behavior of this product in soil. One of the important characteristics of the fertilizer we prepared is slow-release property. It is well known that almost all of the urea would quickly dissolve in water after being added into soil, and then the nitrogen is released completely during several days. As is shown in the chart, nitrogen was released to 80% after 60 days, which was raised the utilization of Urea remarkably. The PMSF connected with the soil particle [13,14], at the effect of the soil, the nitrogen was released. These results indicate that the slow-release

property of the product conforms to the standard of slow-release fertilizers of the Committee of European Normalization (CEN)[15].

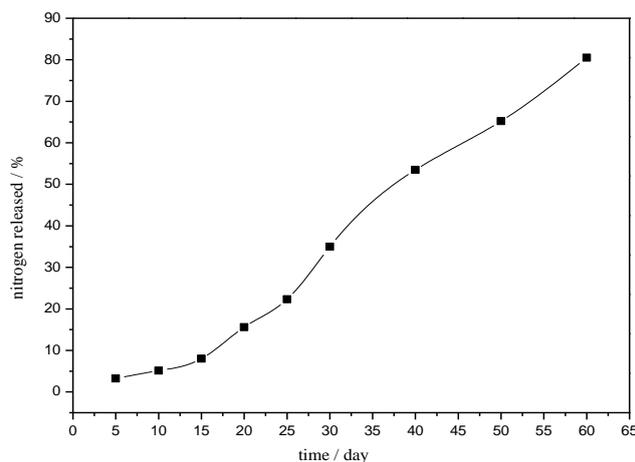


Figure 5. Nitrogen slow-release behavior in soil

3.6 CV curves of the electrochemical polymerization system

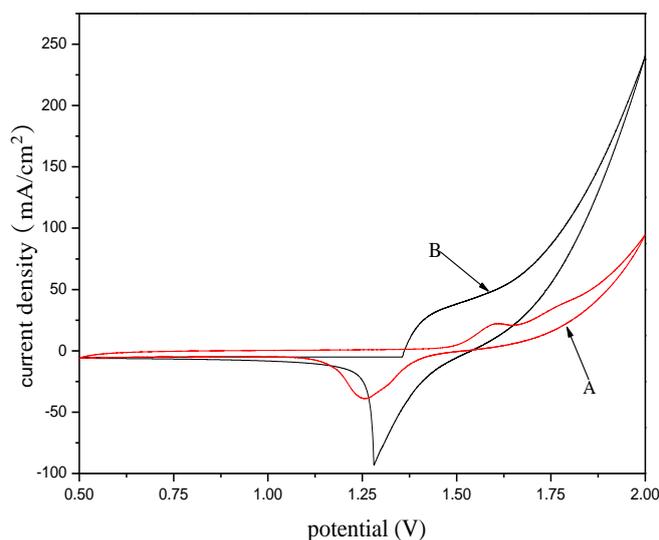


Figure 6. CV curves of the electrochemical polymerization system ($v=50\text{mV}\cdot\text{S}^{-1}$)

Fig. 6 shows the CV curves of the polymerization process and grafting process. Curve A indicates the polymerization process of acrylamid and acrylic acid. Curve B shows the grafting process of Urea and Poly(AM-co-AA).

In the curve A there is an obvious oxidation peak at 1.59V, which shows the oxidation process of Ce(III). According to the standard electrode potential ($E^0[\text{Ce(III)/Ce(IV)}]=1.61\text{V}$), the oxidation products is Ce(IV). It is the oxygen evolving process when the potential is more than 1.6V. When

returns to scan, we can get a reduction peak at 1.20V, which is the reduction reaction of Ce(IV). The curve A proved that the whole polymerization reaction process is quasi-reversible.

In the curve B, the oxidation peak at 1.35V is the oxygen adsorption. The adsorption product is free radicals(\cdot OH). When returns to scan, the reduction peak was found at 1.30V, which is the reduction reaction of Ce(IV). The oxygen evolving process was occurred more than 1.70V.

The study showed that the combined action of initiator and electrochemistry generated a great number of free radicals(\cdot OH) in the electrochemical system[16,17]. These free radicals initiated acrylamide and acrylic acid to Poly(AM-co-AA), then it grafted Urea form to PMSF.

4. CONCLUSIONS

A new type of poly (acrylamide-co- acrylic acid) macromolecule slow-release fertilizer was prepared by electrochemical methods.

The best technological parameters of the process were obtained: $\omega(\text{AM})=9\%$, $\omega(\text{AA})=4.1\%$, $\omega(\text{Ce(IV)})=1\%$, $I=0.05 \text{ A/cm}^2$, $\omega(\text{Urea})=7.2\%$, $\omega(\text{KH}_2\text{PO}_4)=5.4\%$. The total contents of the nitrogen, phosphorus and potassium in the PMSF can achieve a content of 58.5%. Among which, nitrogen 32.5%, phosphorus 13%, potassium 13%.

The study will provide a new method to the filed of the polymer. Other while, the study will enrich the theory of electrochemistry.

ACKNOWLEDGEMENTS

This work is financially supported by the National Natural Science Foundation of China. (No.20771080) and the Technological Project of Shanxi Province. (20100311033).

References

1. B. Ni, M. Z. Liu, S. Y. Lv. *Chem. Engin. J.*155(2009)892.
2. S.M. Al-Zahrani, *Industrial Engin. Chem. Res.*. 39(2000)367.
3. M.Y. Guo, M.Z. Liu, R.Liang, et al. *J. Appl. Polymer Sci.*. 99(2006)3230.
4. S. I. Volfkovich. *J. Appl. Electrochem.*. 45(2009)2479.
5. G. J. Roberts. *American Ceramic Society Bulletin.* 54(1975)1069.
6. Q. X. Wen, Z. Q. Chen, Y. Zhao, H. C. Zhang, *J. Hazard. Mater.*, 175(2010) 955.
7. S. K. Basu, N. Kumar, J. P. Srivastava. *Simulation Modelling Practice and Theory.*18(2010) 820.
8. R. Liang, M.Z. Liu. *Journal of Agricultural and Food Chemistry.* 54(2006)1392.
9. K. Partha, Chandra, G. Kunal, V. Chandrika. *Chem. Engin. J.* 155(2009)451.
10. Z. H. Liang, R. P. Wang, C. M. Fan, *J. Rare Earths.* 25(2007) 91.
11. J. A. Entry, R. E. Sojka, B. J. Hicks, *Geoderma*, 145(2008)8.
12. B. Grassl, G. Clisson, A. Khoukh, L. Billon, *European Polymer J.*, 2008,44: 50-58.
13. F. L. Buchholz, A. T. Graham. *Wiley-VCH*, New York,1998.
14. U. Shavit, M. Reiss, A. Shaviv. *J. Controlled Release*, 88(2003)71.
15. M.E. Trenkel, *Stratospheric Ozone, HMSO*, 1997.
16. U. Shavit, A. Shaviv, G. Shalit, D. et al. *J. Controlled Release*, 43(1997)131.
17. J. P. Zhang, A. Li, A. Q. Wang, *React Funct Polym.* 66(2006)747.