Preparation and Properties of Graphene Oxide Modified Nanocomposite Hydrogels

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Abstract. Nanocomposite hydrogels with graphene oxide as chemical cross-linker were synthesized after graphene oxide being pretreated by methacyryloyl chloride. Moreover, the mechanical behavior of nanocomposite hydrogels based on acrylamide (AAm) and graphene oxide (GO) was studied with different compositions. Experimental results of the swollen state properties of the nanocomposite hydrogels indicated that the addition of GO could effectively enhance the strength but lowers the swelling degree of nanocomposite hydrogels.

1. Introduction

The design and preparation of hydrogels have attracted a great deal of interest in biomedical engineering and biomaterials science because of their tunable chemical and physical structures, high water content and biocompatibility. Since hydrogels are prepared from hydrophilic polymer matrices that are cross-linked by physical or chemical cross-linking, hydrogen bonds, crystallized domains, hydrophobic interactions and chemical cross-linkers have been utilized for the synthesis of different types of hydrogels.

In recent years, nanomaterial has been explored for the preparation of nanocomposite hydrogels. For example, Nano materials, such as Laponite [1-5] and HNTs [6], have been used as the basic framework to obtain enhanced mechanical strength. And with the addition of multiple walls nanotube [7], hydrogels show increased electrical properties with 1.04 ms/cm.

In this study, the preparation of nanocomposite hydrogels based on acrylamide and graphene oxide was investigated by using methacyryloyl chloride as pretreated agent for graphene oxide. And the properties of the nanocomposite hydrogels were characterized by swelling degree and mechanical tests.

2. Experimental

1.1. Chemicals

Graphene oxide was prepared by a modified Hummers method [8]. Acrylamide (AAm), N,N'-methylene bisacrylamide (BIS), Potassium persulfate (KPS), Dimethyl sulfuir dioxide (DMSO), isopropanol, HCl and triethylamine were supplied by Aladdin Industrial Co. (Shanghai, China). Methacryloyl chloride (purity 99%) was purchased from Sun Chemical Technology (Shanghai, China) Co. Ltd. and used as received.
1.2. Synthesis of modified graphene oxide

After 0.5 g of GO was dispersed in 200 ml of DMSO by ultrasonic treatment for 10 min, 4.8 ml of triethylamine was gradually added and the mixture was stirred for another 30 min. Subsequently, 3.4 ml of methacryloyl chloride was added dropwise in an ice-salt bath at 0 °C. After stirring for 2 h, the temperature of the suspension was raised to 45 °C, which was maintained for another 24 h. Then, the suspension was further diluted by adding 100 ml of isopropanol. The mixture was filtered and washed with HCl and deionized water until the pH was 7. Finally, the resulting solid was dried under freeze drying at -50 °C for 48 h to obtain modified graphene oxide. The as-prepared graphene oxide was named as GOM.

1.3. Synthesis of nanocomposite hydrogels

0.3 g of GOM in 15 ml of deionized water was ultrasonically dispersed for 10 min in ultrasonic cleaning bath at room temperature. 1.8 g of AAm monomer was added with stirring and maintained there for another 10 min. Then, the initiator (0.5% KPS) was added into the mixture and bubbled with high purity argon for 10 minutes. The resultant sample solution was poured into the space between two glass plates with a 2 mm silicone rubber as a spacer. Heat-initiated polymerization was carried out at 60 °C for 24 h.

For comparison, AAm solution with BIS as cross-linker was also prepared with the same initial monomer and initiator concentration.

1.4. Characterization and measurements

The water content of nanocomposite hydrogels was evaluated in terms of the swelling ratio. The swollen nanocomposite hydrogels were cut into small pieces and weighed at regular intervals until equilibrium was reached. Then, these hydrogels were carefully deswollen in a series of water-alcohol mixture with increasing alcohol contents until all samples were dried under vacuum to constant weight. The swelling degree (SD) of the nanocomposite hydrogels was determined by the equation:

\[ SD = \frac{m_t - m_0}{m_t} \times 100\% , \]

where \( m_t \) and \( m_0 \) are the weights of swollen and dry hydrogels, respectively.

The compressive stress-strain measurements were performed to the equilibrium swollen hydrogels, using a tensile-compressive tester (Regger 3010, Orientec Co.). The average values of stress-at-break and strain-at-break of the nanocomposite hydrogels were then determined from the mechanical stress data.

3. Results and Discussion

3.1 Graphene oxide modified nanocomposite hydrogels
Figure 1. Photographs of nanocomposite hydrogels and PAAm hydrogels. (a) PAAm hydrogels (b) graphene oxide modified nanocomposite hydrogels.

Nanocomposite hydrogels based on AAm and GO were investigated by using methacryloyl chloride as pretreated agent for graphene oxide. Since GO sheet is a single-layer graphite sheet with several hydrophilic oxygenated functional groups, the carboxyl groups were chosen to interact with methacryloyl group in the pretreated reaction. It is thought that the presence of the double bond on GO sheets can act as a good chemical cross-linker for the synthesis of different types of hydrogels. In the GO-based hydrogels photographs shown in Figure 1, it can be seen that graphene oxide modified nanocomposite hydrogels are black with good flexibility and recoverability.

3.2 Swelling property of nanocomposite hydrogels

In order to have insights into the water transport process through the GO-based hydrogels, the dependence of the swelling degree on the increase of time was given in Figure 2. It can be seen that comparing with hydrogels using BIS as cross-linker, graphene oxide modified nanocomposite hydrogels exhibit a decreased swelling capacity in pure water. Moreover, the maximum values of swelling degree for graphene oxide modified nanocomposite hydrogels are only about 80%.

3.3 Compression tests

To explore the effect of nanoparticles on mechanical strength of hydrogels, the Stress-at-break of hydrogels was plotted against different cross-linkers of hydrogels, respectively (Figure 3). It is clear that with the addition of graphene oxide as cross-linker, nanocomposite hydrogels exhibit the toughness without obvious fracture even at 90% strain under increased compresses, while BIS crosslinked PAAm hydrogels fractured with the stress of 25%. It seems that in the nanocomposite hydrogels, graphene oxide not only works as the chemical cross-linker, but also greatly improves the elasticity of hydrogels by tangling with PAAm chain.
4. Conclusion

Nanocomposite hydrogels cross-linked by graphene oxide was synthesized by one-step process. Experimental results of nanocomposite hydrogels based on AAm and GO indicated that graphene oxide could be modified and used as chemical cross-linker. Meanwhile, in the compression tests, the results that no obvious fracture appeared even at 90% strain indicated that the existence of graphene oxide might contribute to the physical entanglement of unbonded PAAm chain, which greatly improves the elasticity of hydrogels.

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References

[1] T. Huang, P(NIPAM-co-AA)/clay nanocomposite hydrogels exhibiting high swelling ratio accompanied by excellent mechanical strength, Appl Phys A. 107 (2012) 905–909.

[2] S. Sharifi, S.B.G. Blanquer, T.G. van Kooten, D.W. Grijpma, Biodegradable nanocomposite hydrogel structures with enhanced mechanical properties prepared by photo-crosslinking solutions of poly(trimethylene carbonate)–poly(ethylene glycol)–poly(trimethylene carbonate) macromonomers and nanoclay particles, Acta Biomaterialia. 8 (2012) 4233–4243.

[3] Y.R. Wang, Y.F. Dai, J.H. Gong, J.H. Ma, Preparation and properties of PDMAA/clay nanocomposite hydrogel, Journal of Donghua University(Natural Science). 37 (2012) 671-676.

[4] C.J. Wu, A.K. Gaharwar, B.K. Chan, G. Schmidt, Mechanically tough Pluronic F127/laponite nanocomposite hydrogels from covalently and physically cross-linked networks, Macromolecules. 44 (2011) 8215–8224.

[5] P. Zhang, X.Y. Wang, S.P. Li, H.L. Dai, Nanocomposite hydrogels with high mechanical strength and high swelling ratio by RAFT polymerization, International Journal of Polymeric Materials, 62: 10–16.

[6] M.X. Liu, W.D. Li, J.H. Rong, C.R. Zhou, Novel polymer nanocomposite hydrogel with natural clay nanotubes, Colloid Polym Sci 290 (2012) 895–905.

[7] A.F. Zhu, Z. Shi, J.H. Jin, G. Li, J.M. Jiang, Synthesis and properties of polyacrylamide-based conducting gels with enhanced mechanical strength, Journal of Macromolecular Science R, Part B: Physics. 51 (2012) 2183–2190.

[8] Y.W. Huang, M. Zeng, J. Ren, J. Wang, L.R. Fan, Q.Y. Xu, Preparation and swelling properties of graphene oxide/poly(acrylic acid-co-acrylamide) super-absorbent hydrogel nanocomposites, Colloids and Surfaces A: Physicochem. Eng. Aspects. 401 (2012) 97–106.