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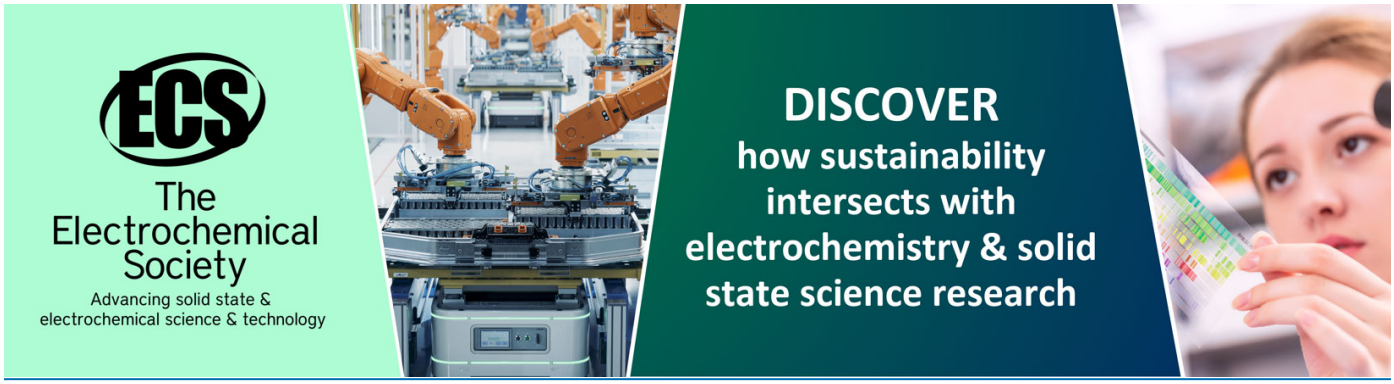

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A pH sensitive graphene oxide/poly (N-methylolacrylamide-methyl acrylate) composite hydrogel

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Abstract. A graphene/poly (vinyl alcohol) composite hydrogel based on poly (N-methylolacrylamide- methyl acrylate) was prepared. The additon of GO evidently change the network structure and enhance the pH sensitivity of hydrogel. The stucture of hydrogel was characterized by SEM and XRD. Factors influencing the swelling behavior of hydrogel were investigated, such as monomer component and GO. In additon, the reversibility of pH sensitivity of hydrogel was studied as well, which will have a good application in drug release field.

1. Introduction

pH sensitive hydrogel achieve lots of attention recently due to their potential application in drug release and artificial muscle.[1] The pH sensitive hydrogel will swell or deswell after changing ambient pH value. These gels commonly contain large amounts of easily hydrolyzed or protonated acid or base groups, such as carboxyl and amino groups. The dissociation degree of these groups influenced by the external pH change may affect the number of cross-linking points within the network, thereby causing changes in volume of the gel. The hydrogel containing acidic groups will swell with the increase of pH. Previous study indicates that a pH sensitive hydrogel prepared from graphene oxide (GO) and poly (vinyl alcohol) (PVA) showed excellent pH sensitive capability[2][3]. Due to the plenty of hydrophilic oxygenated functional groups, GO sheets can uniformly disperse into in PVA matrix and reinforce the hydrogel film by the strong hydrogen bonds between nanosheets and PVA chains, thereby increasing its pH response capability[4]. Herein, we introduce GO/PVA to poly (N-methylolacrylamide- methyl acrylate) system to obtain pH-sensitive composite hydrogel GO-PVA/P(HMAM-MA). Furthermore, we studied the network structure of the hydrogel by scanning electron microscopy (SEM) and the swelling property with different pH value.

2. Results and Discussion

In the experiments, PVA powders completely dissolved in hot water (90 ℃) and then cooled to room temperature to obtain PVA solution. Then GO aqueous solution, monomers, initiator and catalyst were successively added into the PVA solution and subsequently the mixture was placed at room temperature for polymerization. The obtained hydrogel was frozen at -20 ℃ for 20 h and then thaw at room temperature for 4 h, which is called a freezing thawing cycle (freeze-thaw). The hydrogels prepared in this chapter are through 3 times of freezing thawing cycles. Then the hydrogel soaked in

0.1 mol/L NaOH solution for 8 days and next soaked in distilled water for 8 days to obtain pH sensitive hydrogels. The compositions of GO-PVA/P (HMAM-MA) hydrogels were shown in Table 1.

Table 1. the components of GO-PVA/P (HMAM-MA) hydrogels.

Sample	components ratio						
	PVA (g)	GO (mg)	HMAM (g)	MA (g)	KPS (mg)	TEMEM (μl)	H2O (g)
PVA/P(H9-M1)	0.50	0	0.910	0.086	10	8	9.914
GO1-PVA/P(H9-M1)	0.50	10	0.910	0.086	10	8	9.914
GO2-PVA/P(H9-M1)	0.50	20	0.910	0.086	10	8	9.914
GO3-PVA/P(H9-M1)	0.50	25	0.910	0.086	10	8	9.914
GO1-PVA/P(H8-M2)	0.50	10	0.810	0.172	10	8	9.828
GO1-PVA/P(H7-M3)	0.50	10	0.710	0.258	10	8	9.742

PVA/P (H9-M1) hydrogel and GO1-PVA/P (H9-M1) hydrogel were lyophilized and the corresponding SEM images were shown in Figure 1. The dense network structure with 5 μm of pore size for PVA/P (H9-M1) could be seen from Figure 1a. However, the network structure of the hydrogel become larger with 10μm after addition of GO. This is attributed to GO interacting with PHMAM and PVA to form hydrogen bonds, which acts as a large multifunctional crosslinker. Besides, GO may form a micro-channel leading to increase the pore size.

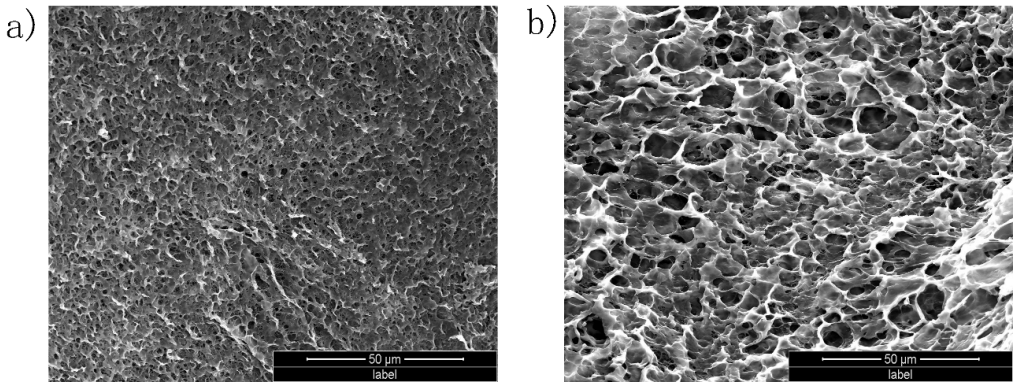

Figure 1. SEM images of (a) PVA/P (H9-M1) hydrogel and (b) GO1-PVA/P (H9-M1) hydrogel

The XRD curves of PVA/P (HMAM-MA) and GO-PVA/P (HMAM-MA) hydrogel shown in Figure 2. It can be seen obviously the diffraction peaks of gel PVA/P (HMAM-MA) in 2θ=19.7 °, 2θ=22.5 ° and 2θ=40.8 °. However, the peak in GO-PVA/P (HMAM-MA) exhibit a wider trend, which attributed to the formation of hydrogen bonds between GO and PVA component. These hydrogen bonds will lead the diffraction peak to a lower degree slightly.

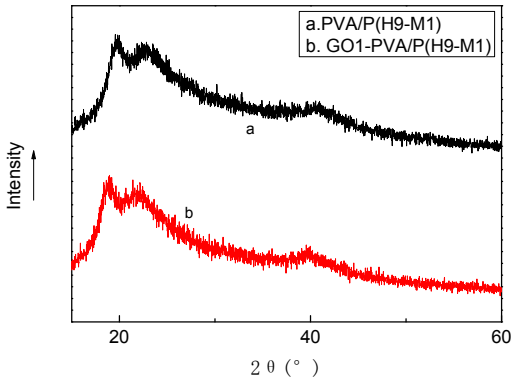

Figure 2. XRD curve of PVA/P (HMAM-MA) and GO-PVA/P (HMAM-MA) hydrogel

Figure 3 showed the swelling curves of GO-PVA/P (HMAM-MA) hydrogels. Balanced swelling ratio (SR) represent the ratio of original volume to swelling volume. It can be seen the influence of content of GO and components on the swelling behavior of hydrogels. The four samples have reached swelling equilibrium after 10 hours in water and the swelling ratio of hydrogel containing GO decreased by 52.94% relative to that without GO. This result is attributed to the hydrogen bonds between GO and PHMAM and PVA act as physical crosslinker to increase the crosslinking density of hydrogel. So, the water molecule is hard to enter the gel and the swelling ratio decreased. In addition, it is obvious that increasing the content of HMAM monomer could lead to the decreased SR of hydrogel. This result is attributed that the GO with a large number of hydroxyl, carboxyl and other hydrophilic functional groups can have a stronger interaction with HMAM monomer. The increase of HMAM would increase the crosslinking points with GO and decrease the pore size of the gel structure, thereby decreasing the hydrogel swelling capability.

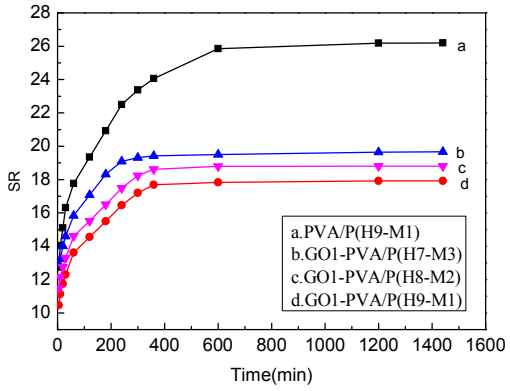

Figure 3. Swelling curves of GO-PVA/P (HMAM-MA) hydrogels.

The equilibrium swelling degree of hydrogel in different pH at 25℃ was shown in Figure 4. It can be seen the equilibrium swelling ratio of four samples increase gradually with the increase of pH value. The equilibrium swelling degree increases slightly in low pH, while it increases obviously with pH above 3. When the pH value reaches 7, the equilibrium swelling degree showed a slight increase. This trend is consistent with pH sensitive hydrogel of PAA and PMAA systems[5]. This is attributed that strong acid condition is necessary for the formation of hydrogen bonds between -COOH and -CONH-. With the increase of pH, the hydrogen bonding is gradually destroyed and -COOH gradually

dissociates into -COO-, which increases the hydrophilicity of hydrogel and promotes the hydrogel swelling. On the other hand, the increase of methacrylate content could improve the pH response capability.

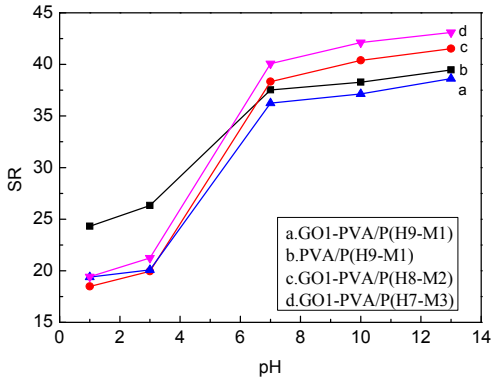

Figure 4. The equilibrium swelling degree of the hydrogels under different pH conditions at 25℃

In order to study the repeatability of the stimulus-response of GO-PVA/P (H7-M3) hydrogel and oscillatory swelling/deswelling tests were conducted by alternating the pH (pH=1 and 7) at 25℃. Figure 5 shows pH cyclic response curves of the hydrogel and it is observed that the sensitive hydrogel shows good reversible response by changing the pH repeatedly. In each cycle, the swelling/deswelling ratio of the pH response decreased from the first to the second run and became stable afterwards.

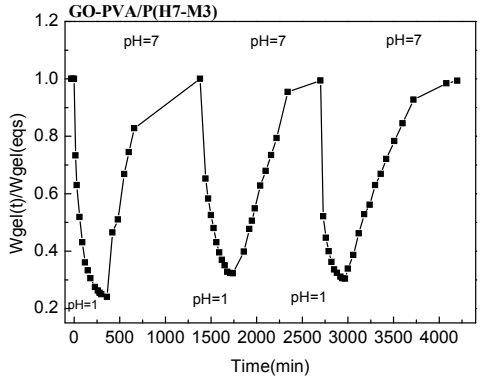

Figure 5. pH cyclic response curves of GO-PVA/P (H7-M3) hydrogels

3. Conclusion

In summary, GO-PVA/P(HMAM-MA) hydrogels prepared in this study showed excellent pH sensitivity. The addition of GO evidently change the network structure of materials and effectively improve the pH sensitivity of hydrogel. Furthermore, this hydrogel exhibits excellent reversible response by changing pH repeatedly, which will have a good potential application in drug release field.

Acknowledgments

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