

# Two-step synthesis of polyacrylamide/poly(vinyl alcohol)/polyacrylamide/graphite interpenetrating network hydrogel and its swelling, conducting and mechanical properties

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**Abstract** Polyacrylamide/poly(vinyl alcohol)/polyacrylamide/graphite interpenetrating network (PAM/PVA/PAM/G IPN) hydrogel is synthesized using a simple two-step polymerization method. The swelling behaviors of the hydrogel depend on the PVA, graphite, and crosslinker dosages, and swelling process is dominated by a relaxation of macromolecule chains. Owing to IPN structure, the hydrogel shows a good mechanical strength and thermal stability. On the other hand, the incorporation of graphite improves the conductivity of the hydrogel.

## Introduction

Hydrogel polymers, such as polyacrylamide (PAM), are structurally loosely cross-linked network hydrophilic polymers [1], which have the ability to absorb considerable amounts of water or aqueous fluids to form a stable hydrogel, and the absorbed water is hardly removed under some pressure. About three decades ago [2, 3], hydrogel polymers were introduced into the agriculture and diaper industries, and then their applications were extended to other industries where an excellent water-holding property was emphasized. Recently, many researchers focus their attention on the hydrogel polymer to develop new applications, such as conducting materials, biomaterials, sensors, and release materials [4–12]. A multifunctional hydrogel material is expected to be prepared to meet

applications requirement by modifying, grafting, copolymerizing, and other methods.

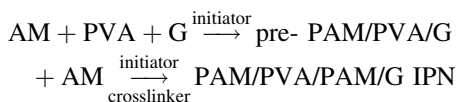
Recently, carbon conducting polymer composites have been developed, which mainly concentrated on adding graphite [13], carbon fibers [14], carbon black [15], and carbon nanotubes [16] to polyethylene, nylon, esters, etc. These conducting composites are mostly solid state. On the other hand, conducting hydrogels [17–19], typical quasi-solid materials, have not been developed. Based on the electrical conductivity of graphite and the water absorbency of polymer matrix, it is significant to add graphite particles to polyacrylamide/poly(vinyl alcohol) (PAM/PVA) to form a composite with a better hydrogel conductivity. A conducting hydrogel could be used in fuel cells, supercapacitors, dye sensitive solar cells, and rechargeable lithium batteries [20, 21], due to its better conductivity property, colloid stability, low cost, and simple preparation.

Despite their high potential as multifunctional materials, the low mechanical strength of hydrogels is a disadvantage for practical applications. Therefore, much attention has been paid to establish a useful method to create tough hydrogels, such as introducing dangly comb-chains [22], adding polymer particles in gel network [23], cold treating [24] or freeze-drying [25], incorporating clay with polymer [26], forming interpenetrating network (IPN) structure [27]. The formation of a full IPN network structure is believed to be an effective method for enhancing the mechanical strength of hydrogel. Gong et al. [28] succeeded in creating a tough double network hydrogel, which is a kind of IPN structure prepared by the following two-step gel formation: the first step is gelation of rigid polyelectrolyte (the first network), and in the second step flexible neutral polymers (the second network) are introduced in the first network. The IPN hydrogels, containing

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90% water, exhibit compressive fracture strength of more than 20 MPa and a rather high Young's modulus (ca. 0.1 MPa). This is similar to the second-generation superporous hydrogel hybrids (SPH). Omidian et al. [4] has demonstrated in detail the developments of SPHs. Owing to the poor mechanical and elastic properties for the second-generation SPH, the third generation of SPHs is necessarily to be developed. Unlike SPH composites (the second generation of SPHs) wherein a pre-crosslinked matrix-swelling additive is added [29], SPH hybrids are synthesized using a hybrid agent that can be crosslinked after SPH is formed. The hybrid agent is a water-soluble or water-dispersible polymer that can form crosslinked structure through chemical or physical crosslinking. PVA is a typical water-soluble hybrid agent used in preparing IPN hydrogels. Once the second network is formed, the whole system becomes an IPN system. But the method is moderately complicated.

In this paper, a simple two-step polymerization method is used for the synthesis of PAM/PVA/PAM IPN structure; subsequently graphite particles are introduced into the system to form a novel conducting hydrogel with a high mechanical strength. The synthesis process is shown in the following expression. The unusual swelling and mechanical properties are investigated in detail.



## Experimental

### Materials

Acrylamide (AM) monomer was used as received. Potassium peroxydisulfate (KPS) was a radical initiator for the synthesis reaction of PAM and PVA. *N,N'*-methylene bisacrylamide (NMBA), a crosslinker for preparation of the IPN structure, was purified by recrystallization from 66 wt% ethanol/water solution. PVA was used without further purification and graphite micropowders having a specific surface area larger than  $80 \text{ m}^2 \text{ g}^{-1}$  and an average particle size smaller than  $1.6 \times 10^{-6} \text{ m}$  were dried at  $105 \text{ }^\circ\text{C}$  for 4 h prior to use. The above materials were all purchased from Shanghai Chemical Reagents Co., China.

### Preparation of PAM/PVA/PAM/G composites

In a typical synthesis, a mixed solution consisting of AM monomers and PVA was prepared by dissolving desired amounts of AM and PVA in 30 ml distilled water for 3 h at  $90 \text{ }^\circ\text{C}$ . A predetermined amount of graphite micropowders was dispersed in the above mixture. The mixture solution

was stirred and heated at  $80 \text{ }^\circ\text{C}$  in a water bath for 30 min, under a nitrogen atmosphere. Initiator KPS was added into the solution, and the prepolymerization reaction was carried out until the viscosity of the reactant hybrid solution becomes  $140 \text{ mPa s}$ . Another prepared mixed solution consisting of 5 g AM monomer and NMBA in 5 ml distilled water was poured into the above prepolymerization solution, and the initiator KPS was added again. Under a nitrogen atmosphere, the mixture solution was stirred until the viscosity of the diluted mixed reactant solution reached around  $180 \text{ mPa s}$ . Thus the dope was transferred to room temperature and polymerized equably. The half productions were rinsed with distilled water and dried under vacuum at  $80 \text{ }^\circ\text{C}$  for more than 12 h to a constant weight to remove oligomers and any impurities. After being milled and sifted using a 40-mesh screen, a powdered product PAM/PVA/PAM/G IPN composite was obtained.

### Measurements of swelling ratio and electrical conductivity of the IPN hydrogels

Measurements for swelling ratio of the hydrogels were carried out in distilled water at  $25 \text{ }^\circ\text{C}$ . Each experiment was repeated three times with errors of approximately  $\pm 4.5\%$ , and the swelling ratios (SR, g/g) were calculated at certain intervals according to the equation below:

$$\text{Swelling ratio (SR)} = \frac{W_2 - W_1}{W_1}, \quad (1)$$

where  $W_1$  is the weight of dried composite (g) and  $W_2$  is the weight of swollen hydrogel (g).

The powdered composite of 3 g was immersed in distilled water of 500 ml at room temperature for at least 3 h to reach swelling equilibrium, which resulted in the absorption of water inside the network of the composite and the formation of a conducting hydrogel. The unadsorbed water was removed by filtering over a 40-mesh stainless steel screen and hanging up for 25 min. The electrical conductivity of the hydrogel washed for three times was measured by inserting a Pocket Conductivity Meter (HANNA8733) in a cylinder containing a swollen sample of 30 g.

### Measurement of mechanical strength

The mechanical properties of hydrogels were measured using Dejie DXLL-20000 equipment. The test conditions were controlled as follows: temperature  $25 \text{ }^\circ\text{C}$ ; the sample length of 80 mm; crosshead speed of  $100 \text{ mm min}^{-1}$ . The cubic samples were elongated at a strain rate of  $5\% \text{ min}^{-1}$ . The strain under stress was defined as the change in length relative to the initial length of the specimen. The tensile strength and modulus were calculated on the basis of the

initial cross section. The tensile strength or strain of hydrogel was obtained according to the following equation:

$$\sigma = \frac{F}{A}, \quad (2)$$

where  $\sigma$  is tensile strength or strain,  $A$  is cross-sectional area of zonal hydrogels,  $F$  is the force acted on the sample.

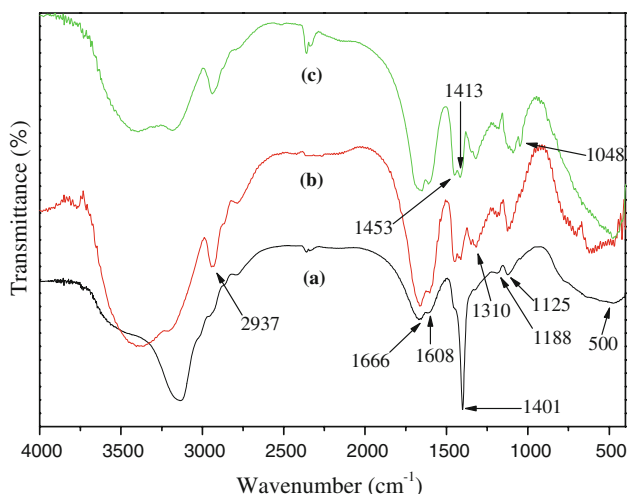
### Characterizations

The powdered sample was identified by IR spectroscopy on a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets. The thermal stability was also carried out on a thermogravimetric analyzer (TA5200, USA) by heating the polymer samples at a rate of  $15\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen atmosphere. The thermal studies were conducted in the temperature range between room temperature and  $700\text{ }^{\circ}\text{C}$ .

## Results and discussion

### Characterizations

The FTIR spectra of PAM, PAM/PVA/PAM, and PAM/PVA/PAM/G composites are shown in Fig. 1. For PAM, the broad, strong band at  $3700\text{--}3000\text{ cm}^{-1}$  is due to O–H stretching in H–O–H, while the aminogroup ( $\text{--NH}_2$ ) stretching also appears in this wavenumber range, i.e., the O–H and  $\text{--NH}_2$  peaks overlap here. The absorption peaks at  $2937$ ,  $1666$ ,  $1608$ ,  $1310$ , and  $1401\text{ cm}^{-1}$  are due to  $\text{--CH}_2$ -asymmetrical stretching vibration, C=O stretching (AM band I), N–H in-plane bending in  $\text{--CONH}_2$  group (AM band II), C–H bending, and C–N stretching vibration, respectively. The peaks at  $1188$  and  $1125\text{ cm}^{-1}$  correspond



**Fig. 1** FTIR spectra of (a) PAM, (b) PAM/PVA/PAM, and (c) PAM/PVA/PAM/G

to  $\text{--NH}_2$  in-plane rocking vibrations and the broad band at  $500\text{ cm}^{-1}$  is attributed to  $\text{--NH}_2$  out-plane rocking vibration peak [30].

For PAM/PVA/PAM and PAM/PVA/PAM/G composites, the absorption peak at  $1453\text{ cm}^{-1}$  is due to C–H,  $\text{--CH}_2$ -, and O–H bending. Compared to pure PVA and PAM, O–H stretching vibration peak in PAM/PVA/PAM and PAM/PVA/PAM/G shifts to higher frequency, the absorption peak at  $1401\text{ cm}^{-1}$  derives two weak peaks at  $1453$  and  $1413\text{ cm}^{-1}$ , and the peak at  $1125\text{ cm}^{-1}$  also moves to  $1048\text{ cm}^{-1}$ . The above changes are due to the appearance of OH free radical and its partial copolymerization with AM monomer. In PAM/PVA/PAM/G spectrum, a new absorption peak that is due to C–O–C stretching vibration at  $1048\text{ cm}^{-1}$  appears. The appearance of the ether group reveals intermolecular and intramolecular self-crosslinking [31].

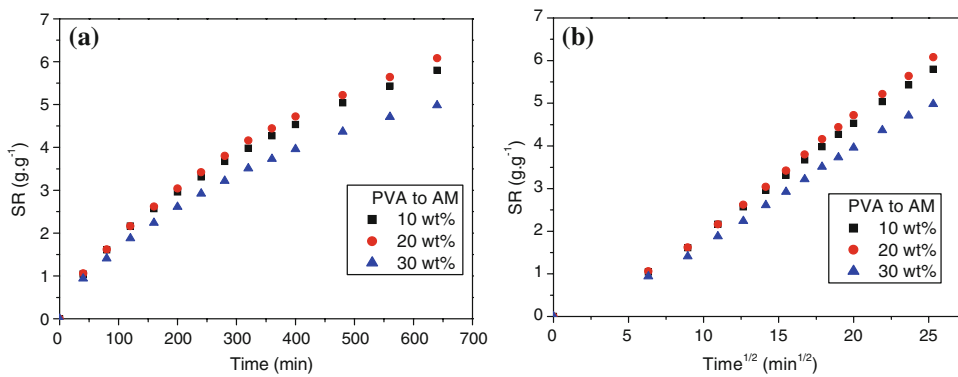
### Swelling kinetics

The influences of PVA, graphite, and crosslinker dosages on swelling rate of the hydrogels are shown in Figs. 2–4. It can be seen that they have similar swelling tendency. This indicates that the dosages of components have no obvious effect on the swelling behaviors of the hydrogels. However, finally SR of the hydrogel changes with changing of PVA, graphite, and crosslinker contents. PVA is a multihydroxy polymer. When it is combined with PAM to form an IPN structure, there will be intermolecular hydrogen bonds between PVA and PAM, which will affect the swelling behaviors of PAM/PVA/PAM/G IPN hydrogels. Wu et al. [32] have adjusted in detail the hydrophilic groups to obtain high water absorbency on starch-graft-acrylamide/mineral superabsorbent composite. They revealed that the collaborative absorbent effect of  $\text{--CONH}_2$ ,  $\text{--COONa}$ , and  $\text{--COOH}$  groups is superior to that of single  $\text{--CONH}_2$ ,  $\text{--COONa}$ , or  $\text{--COOH}$  group. When the composite has a proper ratio for the groups, the highest water absorbent ability is obtained. Similarly, the collaborative effect of  $\text{--OH}$  group in PVA and  $\text{--CONH}_2$  group in PAM is the best when the mass ratio of PVA to AM is 20 wt%, and thus, the equilibrium SR is the highest (Fig. 2a).

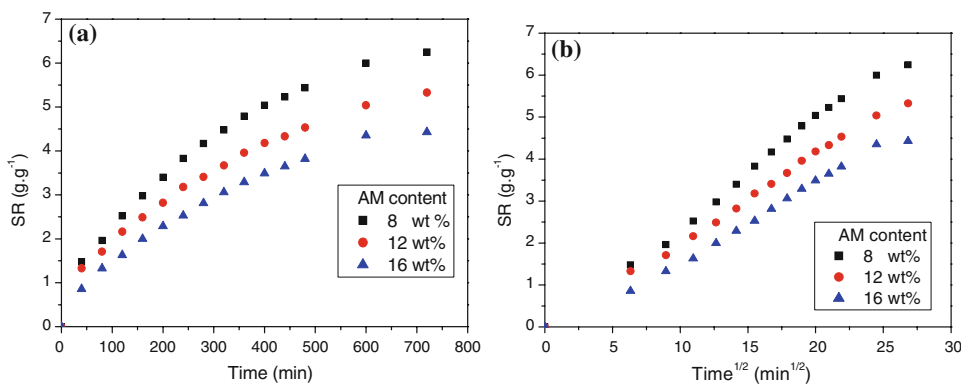
The natural graphite powder is hydrophobic; the introduction of graphite inevitably decreases the hydrophilic ability and equilibrium SR, as can be seen from Fig. 3a.

Crosslinker is another important parameter for SR of the hydrogels. Clearly, the integration of PVA and PAM and the formation of three-dimensional (3D) network of the polymer depend on the crosslinker amount. Under lower crosslinker concentrations, the polymerization reaction does not occur adequately, and the 3D network of the polymer does not form effectively; water molecules cannot be held in the 3D network, which leads to the decrease of

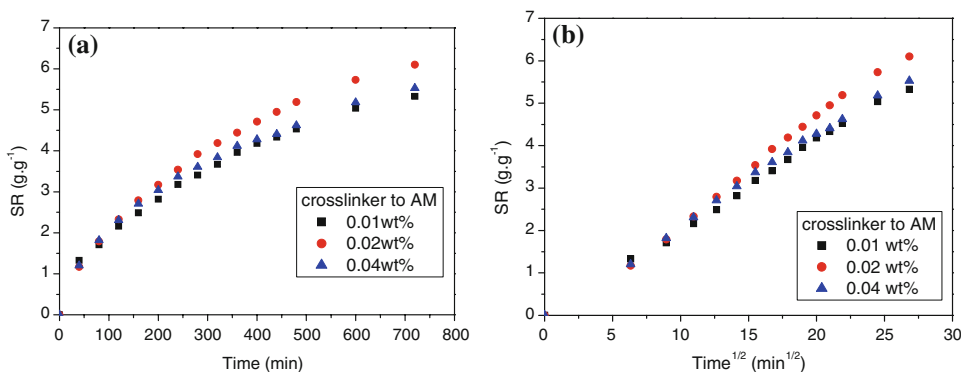
**Fig. 2** The SR of the hydrogels with mass ratio of PVA to AM 10 wt%, 20 wt%, and 30 wt% as a function of swelling time (preparation conditions: 0.01 wt% crosslinker, 0.8 wt% initiator, and 12 wt% graphite)



**Fig. 3** The SR of the hydrogels with mass ratio of graphite to AM 8 wt%, 12 wt%, and 16 wt% as a function of swelling time (preparation conditions: 0.01 wt% crosslinker, 3 wt% initiator, and 20 wt% PVA concentration)



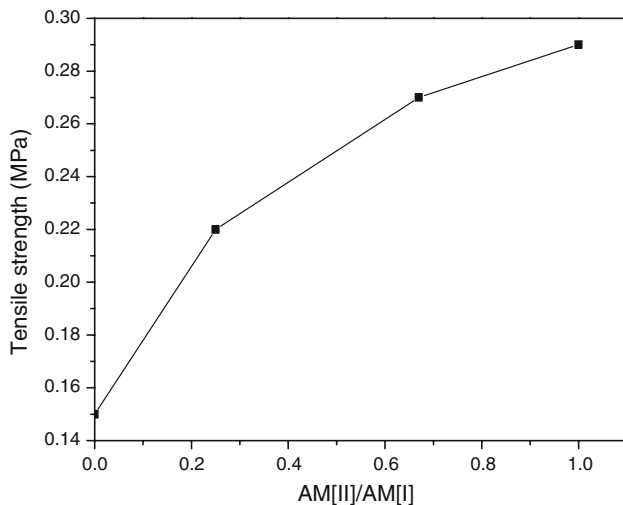
**Fig. 4** The SR of the hydrogels with mass ratio of crosslinker to AM 0.01 wt%, 0.02 wt%, and 0.04 wt% as a function of swelling time (preparation conditions: 0.15 wt% initiator, 12 wt% graphite, and 20 wt% PVA)



the SR. On the other hand, a higher concentration of crosslinker produces a larger number of growing polymer chains, which are in turn involved in generating an additional network [33]. Thereby, SR decreases with an increase in the crosslinker concentration because the network space gets diminished and less water enters the composite. Furthermore, in comparison with traditional hydrogels or superabsorbents, the swelling process to reach equilibrium state is prolonged. This may be the result of interpenetration and entanglement of PAM and PVA networks, which restrict the expansion and swelling of PAM/PVA/PAM/G hydrogel.

It is known that swelling of hydrogel is a complicated process. Generally, three continuous processes are involved [34]: (1) water molecules enter the inside of

hydrogel, (2) relaxation of macromolecule chains, and (3) stretch of whole macromolecular chains in water. If the first process is dominating in swelling of hydrogel network, the SR is directly proportional to square root of absorption time. If the second process is dominating, the relation plotted in SR and square root of time is “S” figure [35, 36]. From the above three figures plotted by SR versus  $t^{1/2}$ , it can be seen that the shapes describe a S-curve (Figs. 2–4b). Based on that, the second process is dominating in the swelling of PAM/PVA/PAM/G IPN hydrogels. That is the water molecules entering the inside of hydrogel is a fast process, and the relaxation of macromolecule chains is a slow process, which results in the swelling controlled by step (2). The result is consistent with reports [35].

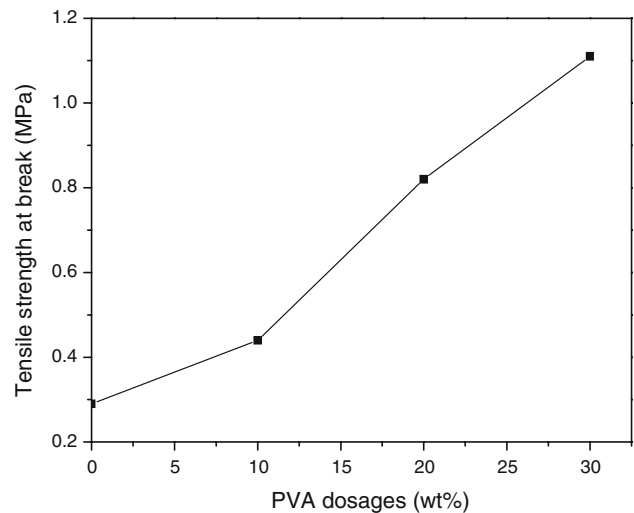


**Fig. 5** Tensile strength of PAM/PVA/PAM/G IPN hydrogels as a function of AM [II]/AM [I] (m/m) ratios (0.1 wt% crosslinker, 3 wt% initiator, 20 wt% PVA, and 12 wt% graphite)

### Mechanical strength

It is known that the good mechanical strength roots in the formation of IPN structure and physical entanglement of the two networks. It can be seen from Fig. 5 that the mechanical strength of PAM/PVA/PAM/G IPN hydrogel increases gradually from 0.15 to 0.29 MPa with the increase of AM [II] contents from 0 to 1 (AM [II]/AM [I], m/m) (AM dosage in the first and second polymerization reaction is designated as AM [I] and AM [II], respectively). It is well known that the IPN structure is not formed without the second component. Therefore, if the whole system becomes a single component, the mechanical strength of the hydrogel decreases dramatically. With the increase of AM [II], the 3D network of PAM [II] tends to be perfect and the IPN structure is also formed. The physical and chemical interactions between PAM [I]/PVA and PAM [II] are also enhanced; especially the physical entanglement is increased. The result is the increase of whole hydrogel strength.

Figure 6 is a representative mechanical strength plot of the PAM/PVA/PAM/G IPN hydrogels with different mass ratios of PVA to AM. As can be seen in Fig. 6, the tensile strength of the hydrogels at break increased gradually with the increase of PVA amounts. It is well known that the excellent mechanical strength roots in the network of PAM, the self-crosslinked network of PVA, and the entanglement of the two networks. In order to investigate the contributions of the first network and the second one, Tsukeshiba et al. [37] have analyzed in detail a double network hydrogel based on poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) and PAM, which were the first and second component, respectively. The experiment results



**Fig. 6** Tensile strength of PAM/PVA/PAM/G IPN hydrogels as a function of PVA content (0.1 wt% crosslinker, 3 wt% initiator, and 12 wt% graphite)

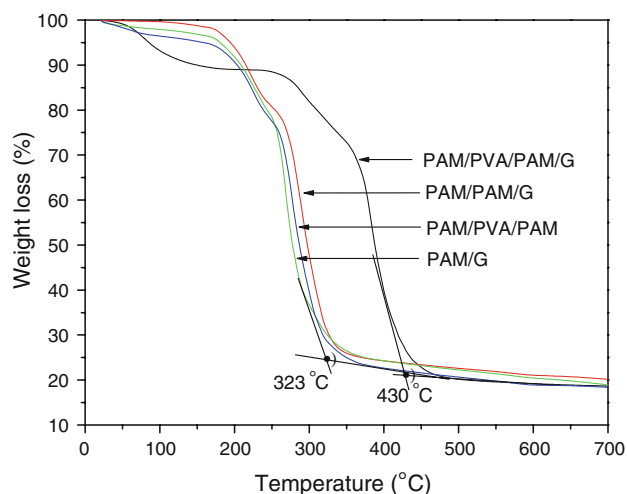
revealed that the first network PAMPS had “voids” with a size much larger than the radius of the second polymer PAM, and the second network in the voids may play a more important role in its inhomogeneous structure model. Similarly, in our conditions, as the first component, PAM hydrogel is a superabsorbent polymer [32, 33], and it has large “voids” with a size much larger than the radius of the second component PVA, which results in the formation of inhomogeneous structure. Therefore, the mechanical strength of the PAM/PVA/PAM/G IPN hydrogels increases with the increase of PVA amount in the hydrogels.

### Conductivity

The PAM/PVA/PAM/G IPN hydrogel shows a conductivity of  $1.4 \text{ mS cm}^{-1}$ . Since the conductivity of swollen PAM/PVA/PAM IPN hydrogel in the same conditions is only  $\leq 1.0 \times 10^{-5} \text{ S cm}^{-1}$ , the observed conductivity from the PAM/PVA/PAM/G IPN hydrogels is mainly accounted for the presence of graphite micropowder component. The result is consistent with conducting hydrogels consisting of polyaniline nanoparticles and pyrrolidone [38], polyaniline–polyacrylamide, and polyaniline–poly(2-acrylamido-2-methyl propanesulfonic acid) semi-interpenetrating network hydrogels [39].

### Thermal stability

Figure 7 depicts a TGA thermogram of the PAM/PVA/PAM/G, PAM/PAM/G, PAM/PVA/PAM, and PAM/G. It can be found that the initial weight loss between 50 and 150 °C is mainly due to the release of moisture from the surface of composites. Further weight loss of PAM/PVA/



**Fig. 7** TGA curves of PAM/PVA/PAM/G, PAM/PAM/G, PAM/G, and PAM/PVA/PAM

PAM/G that takes place at a slower rate between 300 and 350 °C relates to morphological changes in the composite system. The sharp weight loss beginning at about 380 °C presumably corresponds to the large-scale thermal decomposition of PAM/PVA/PAM chains. Gradual weight loss over the wide temperature range can be attributed to the good thermal stability of the PAM/PVA/PAM/G composite. For the TGA curves of PAM/PAM/G, PAM/G, and PAM/PVA/PAM, the tendency is similar to that of PAM/PVA/PAM/G composite except lower decomposition temperature. After complete degradation for both PAM, the weight losses are all around 20%. From the thermal analysis, we can conclude that the physical/chemical interactions of PAM/PVA/PAM/G conducting composite prepared using the simple two-step polymerization technique has excellent thermal stability.

## Conclusions

Polyacrylamide/poly(vinyl alcohol)/polyacrylamide/graphite interpenetrating network (PAM/PVA/PAM/G IPN) hydrogel was synthesized using a simple two-step aqueous polymerization method. The swelling behaviors and the conducting and mechanical properties of the hydrogel are investigated. It is found that the swelling ratio of the hydrogel depends on the PVA, graphite, and crosslinker dosages, and the swelling process of the hydrogel is dominated by a relaxation of macromolecule chains. Owing to IPN structure, the hydrogel has a good mechanical strength and thermal stability. The incorporation of graphite improves the conductivity of the hydrogel.

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