

Molecular dynamic simulations of the water absorbency of hydrogels

Xiang Ou¹ · Qiang Han¹ · Hui-Hui Dai² · Jiong Wang¹

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Abstract A polymer gel can imbibe solvent molecules through surface tension effect. When the solvent happens to be water, the gel can swell to a large extent and forms an aggregate called hydrogel. The large deformation caused by such swelling makes it difficult to study the behaviors of hydrogels. Currently, few molecular dynamic simulation works have been reported on the water absorbing mechanism of hydrogels. In this paper, we first use molecular dynamic simulation to study the water absorbing mechanism of hydrogels and propose a hydrogel-water interface model to study the water absorbency of the hydrogel surface. Also, the saturated water content and volume expansion rate of the hydrogel are investigated by building a hydrogel model with different cross-linking degree and by comparing the water absorption curves under different temperatures. The sample hydrogel model used consists of Polyethylene glycol diglycidyl ether (PEGDGE) as epoxy and the Jeffamine, poly-oxy-alkylene-amines, as curing agent. The conclusions obtained are useful for further investigation on PEGDGE/Jeffamine hydrogel. Moreover, the simulation methods, including hydrogel-water interface modeling, we first propose are also suitable to study the water absorbing mechanism of other hydrogels.

Keywords Hydrogel · Hydrogel-water interface · Water absorbency · Saturated water content · Volume expansion rate

Introduction

A polymer network can imbibe solvent molecules and swell to a large extent when it is put into a solvent. After swelling, the polymer network forms an aggregate called gel. If the solvent is water, the gel is called hydrogel, which is known as cross-linked solutions [1]. A hydrogel consists of a three-dimensional solid network of polymer and imbibes water molecules due to the surface tension effect. Through absorbing or expelling water, hydrogels with various functional groups added along its polymer chain can undergo large and reversible volumetric deformations in response to different external stimuli, such as temperature [2], pH [3], ionic concentration [4], electric field [5–7], and mechanical constraint [8].

In nature, hydrogels can be found in many places, e.g., the cornea in eyes, the connective tissues in human bodies, and many other components of body organisms [9]. Meanwhile, the man-made hydrogels have also been widely applied in many fields. With the property of large volume change and the consequent force, hydrogels can be used as sensors and actuators [10–13]. In many bioengineering applications, such as cartilage replacement [14], scaffolds [15], drug delivery [16], cell targeting [17], cell-immobilization [18], hydrogels have been adopted due to their hydrophilic and biocompatible natures. Applications can also be found in many other areas, like sewage processing [19] and oilfields [20, 21].

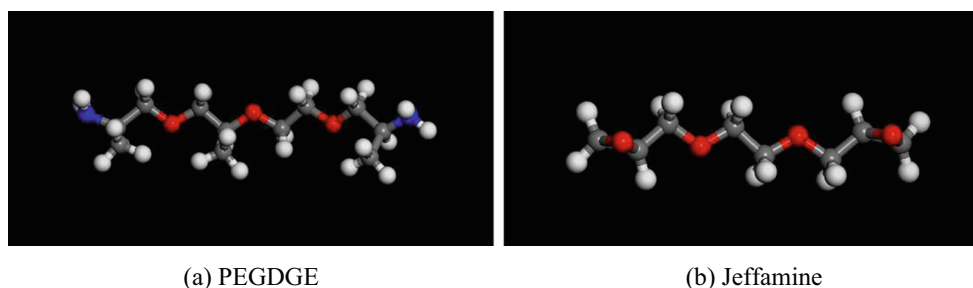
A number of experiments on the water absorption and diffusion of hydrogels have been reported. However, people seldom use molecular dynamic simulation to

✉ Qiang Han
emqhan@scut.edu.cn
Xiang Ou
scut_ouxiang@163.com

¹ School of Civil Engineering and Transportation, South China University of Technology, Guangzhou, Guangdong, People's Republic of China

² Department of Mathematics, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon Tong, Hong Kong

Fig. 1 The models of PEGDGE and Jeffamine (the oxygen, nitrogen, carbon, and hydrogen are marked as red, blue, gray, and white, respectively). **a** PEGDGE **b** Jeffamine



study the same problem. Salahshoor and Rahbar [22] conducted molecular dynamic simulations to study the effect of water on the equilibrated structure and the mechanical properties of cross-linked hydrogel at multiple scales. However, in the study, the structure of hydrogel was directly equilibrated for various volume percent of water content, regardless of water absorbency. Agrawal et al. [23] described a new class of hydrogel composites reinforced with elastic fibers to form a cartilage-like structure. Their experiments measured the saturated water contents of the reinforced and unreinforced hydrogels, but did not describe the water absorbing mechanism of hydrogel. So far there are few research works focused on the water absorbency and absorbing mechanism of hydrogel in a nano-scale. Among those studies of molecular simulations of hydrogel, people just equilibrated hydrogel structure with specific volume percent of water content, ignoring the saturated water contents of hydrogel.

In this paper, we shall propose a hydrogel model, in which the hydrogel consists of Polyethylene glycol diglycidyl ether (PEGDGE) as epoxy and the Jeffamine, poly-oxy-alkylene-amines, as curing agent. Molecular dynamic simulation method is used to study the water absorbency of the hydrogel surface. Also, the saturated water content and the volume expansion rate of hydrogel are investigated by building a

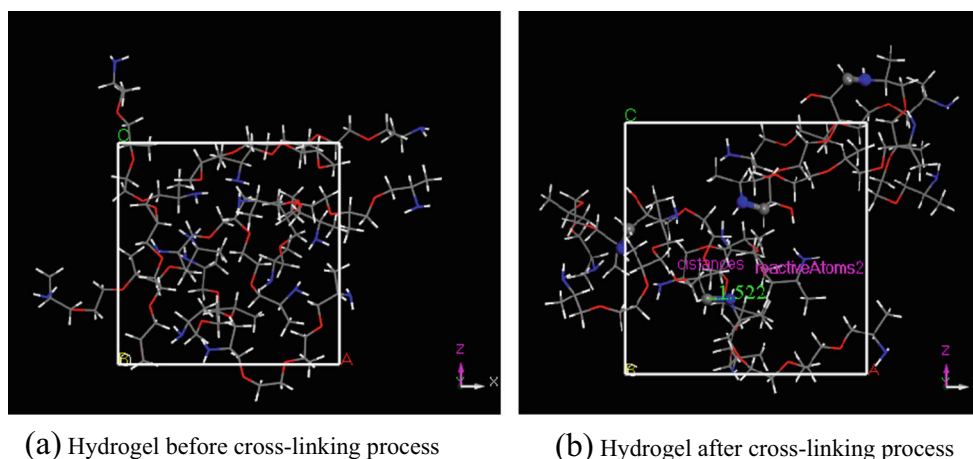
hydrogel model with different cross-linking degree and by comparing the water absorption curves under different temperatures.

Methods

Hydrogel model

The hydrogel consists of Polyethylene glycol diglycidyl ether (PEGDGE) as epoxy and Jeffamine, poly-oxy-alkylene-amines, as curing agent, as shown in Fig. 1. The chemical structure of the PEGDGE and Jeffamine are built separately. A geometry optimization is run to adjust the structure until the total energy is minimized. The charges of each atom are calculated through the self-consistent charge equilibration (QEq) scheme [24]. Then, they are packed into an amorphous unit cell with a PEGDGE-Jeffamine ratio of 1/4 and a density of 1.086 g/cm^3 , as shown in Fig. 2a, using COMPASS forcefield. The lattice parameters of the unit cell are $a=b=c=15 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$. COMPASS is an ab initio forcefield. Most parameters are derived based on ab initio data and the parameters for covalent molecules have been thoroughly validated using various calculation methods including extensive molecular dynamic simulations of

Fig. 2 Hydrogel before and after the cross-linking process. **a** Hydrogel before cross-linking process. **b** Hydrogel after cross-linking process



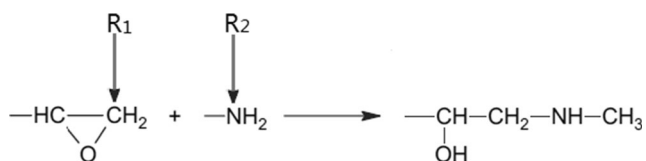


Fig. 3 Principle reaction of PEGDGE and Jeffamine

liquids, crystals, and polymers [25–27]. The forcefield used in all the simulations in this paper is COMPASS.

In addition, all molecular modeling and dynamic simulations are completed by Material Studio.

Before the cross-linking process, a molecular dynamic simulation is run to make the structure of the unit cell equilibrated for 50 ps. Then the cross-linking process is made according to the method developed by Wu and Xu [28] and the reaction shown in Fig. 3. However, from the experimental results, it was found that the cross-linking reaction is a complicated quantum

Fig. 4 Hydrogel-water interface model. **a** hydrogel-water interface model before geometry optimization **b** hydrogel-water interface model after geometry optimization **c** hydrogel-water interface model during water absorption

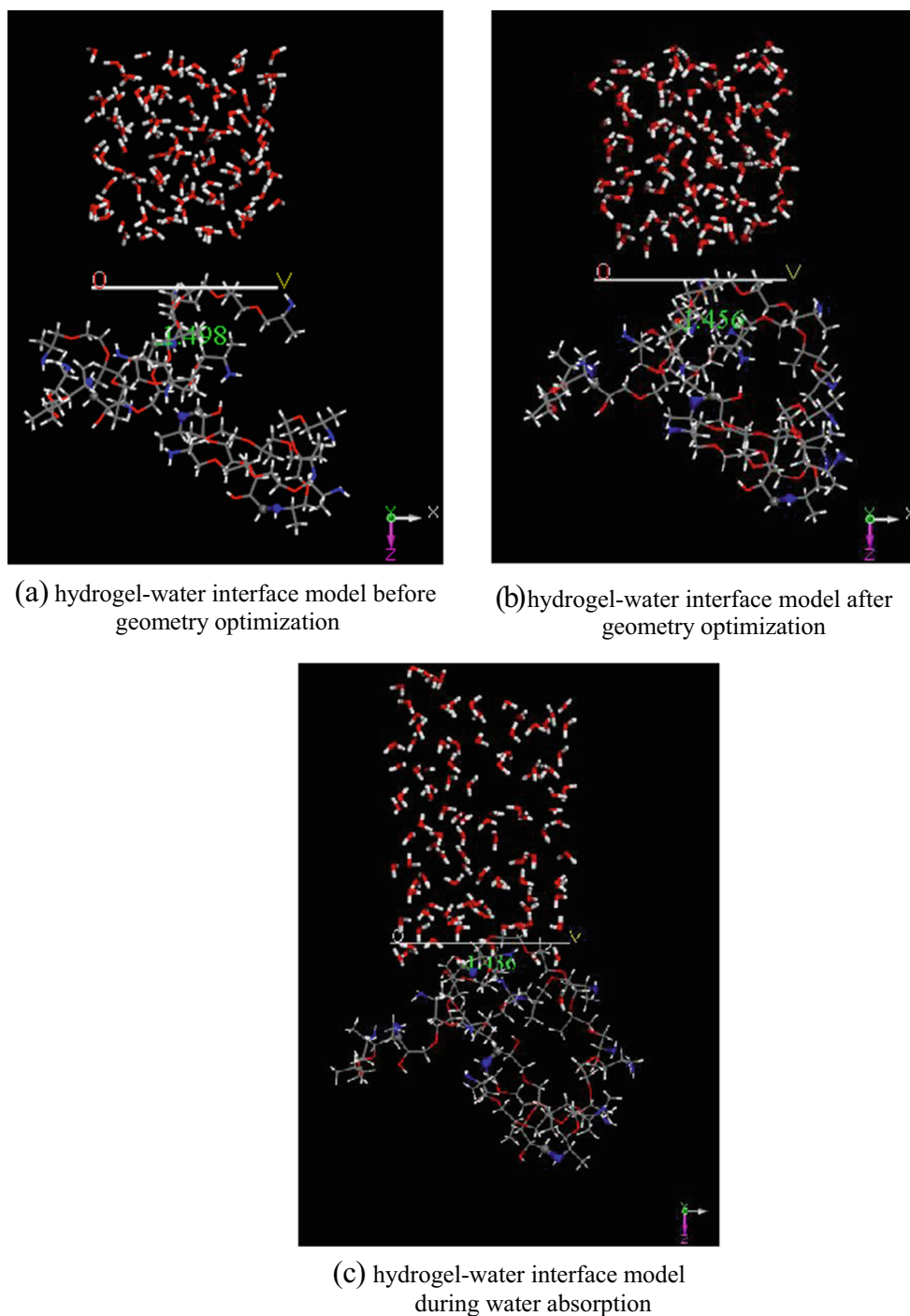
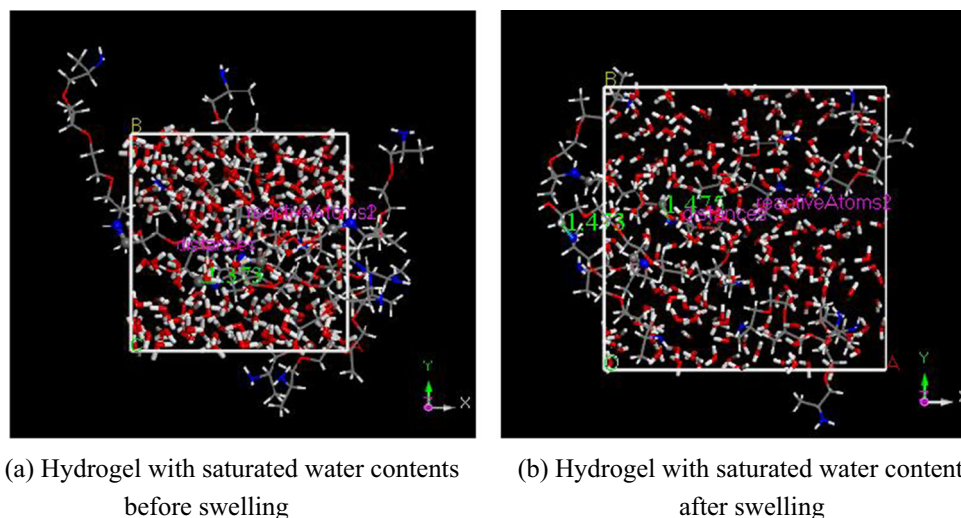


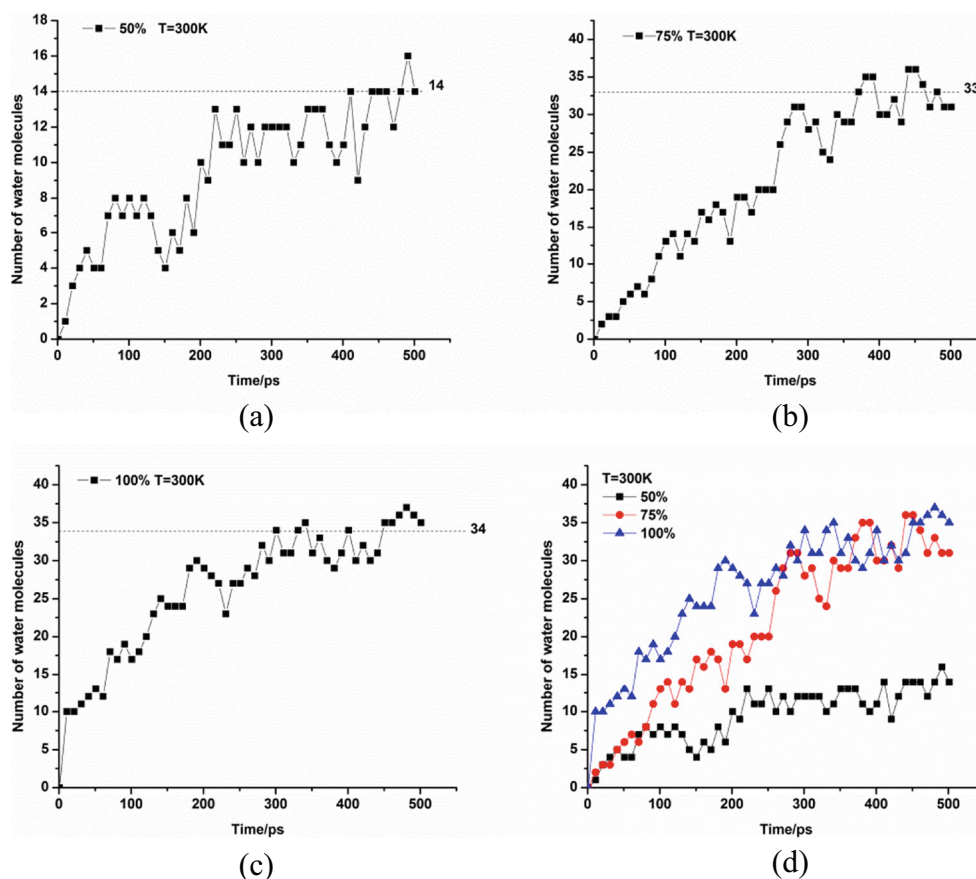
Fig. 5 The swelling of hydrogel.
a Hydrogel with saturated water contents before swelling. **b** Hydrogel with saturated water contents after swelling



mechanical process including the breaking and rebuilding of the bonds and the transfer of the hydrogen atoms. It is difficult to realize this process through molecular dynamic simulation in detail. Therefore, the current work only concerns constructing a cross-linking network close to the reality.

Firstly, we define the reactive atom group as “R1” and “R2” (as shown in Fig. 3). The reactive atom R1 is the carbon atom with two hydrogen atoms on the epoxy. The reactive atom R2 is the nitrogen atom on the amino. Then, an anneal process is used (the ensemble is NPT, and the temperature is raised from target temperature to 500 K, then declined back to

Fig. 6 Water absorption curves of hydrogel-water interface with different cross-linking degree at 300 K



target temperature, the target temperatures we chose in the paper are respectively 300 K, 325 K, 350 K) to make the initial structure more equilibrated. During this process, the initial cutoff distance is set to be 3 Å. When “R1” and “R2” are within the cutoff distance, reaction starts according to the formula shown in Fig. 3, which is realized through the breaking of the bonds between “R1” and oxygen and the forming of new bonds between “R1” and “R2”. Next, another dynamic simulation and anneal process is done to stabilize and equilibrate the structure. After the reaction process, the cutoff distance raised 1 Å and the same process mentioned above is repeated until the cutoff distance attains 10 Å or the degree of cross-linking (the ratio of reacted epoxy to initial epoxy) reaches the expected value. Finally, the hydrogel with specific degree of cross-linking is obtained and it is further equilibrated by using NVT ensemble at the target temperature, as shown in Fig. 2b.

Hydrogel-water interface model

To study the water absorbency of the hydrogel surface, it is necessary to build a hydrogel-water interface model. Firstly, we pack water molecules H_2O into a unit cell with parameters $a=b=c=15$ Å, $\alpha=\beta=\gamma=90^\circ$ and a density of 1.0 g/cm³. A

dynamic simulation (NVT) at the same target temperature (300 K, 325 K and 350 K) of hydrogel is performed to make the water equilibrated. Then a hydrogel-water interface with non-period condition along z-direction and period conditions along x- and y- direction is created as shown in Fig. 4a. The interface is actually the surface located at $z=0$ in Fig. 2b. Next, a geometry optimization is performed to minimize the energy. The obtained hydrogel-water interface is shown in Fig. 4b. After the geometry optimization, the whole structure is equilibrated by using NVT ensemble at the target temperature for 500 ps. The number of water molecules in the hydrogel (or under the interface) N_I is recorded every 10 ps. The saturated water contents of the hydrogel-water interface can be obtained from the water absorption curves shown in Figs. 6, 7, and 8. Figure 4c shows the hydrogel-water interface model during the water absorption.

To simulate the process of water absorption, the hydrogel unit cell should be surrounded by water molecules and equilibrated over time, which means that all six surfaces of the hydrogel shown in Fig. 2b should be the hydrogel-water interfaces and the whole system should be equilibrated for 500 ps. However, it is a very time-consuming task. Therefore, by considering the random distribution of the polymer chains,

Fig. 7 Water absorption curves of hydrogel-water interface with different cross-linking degree at 325 K

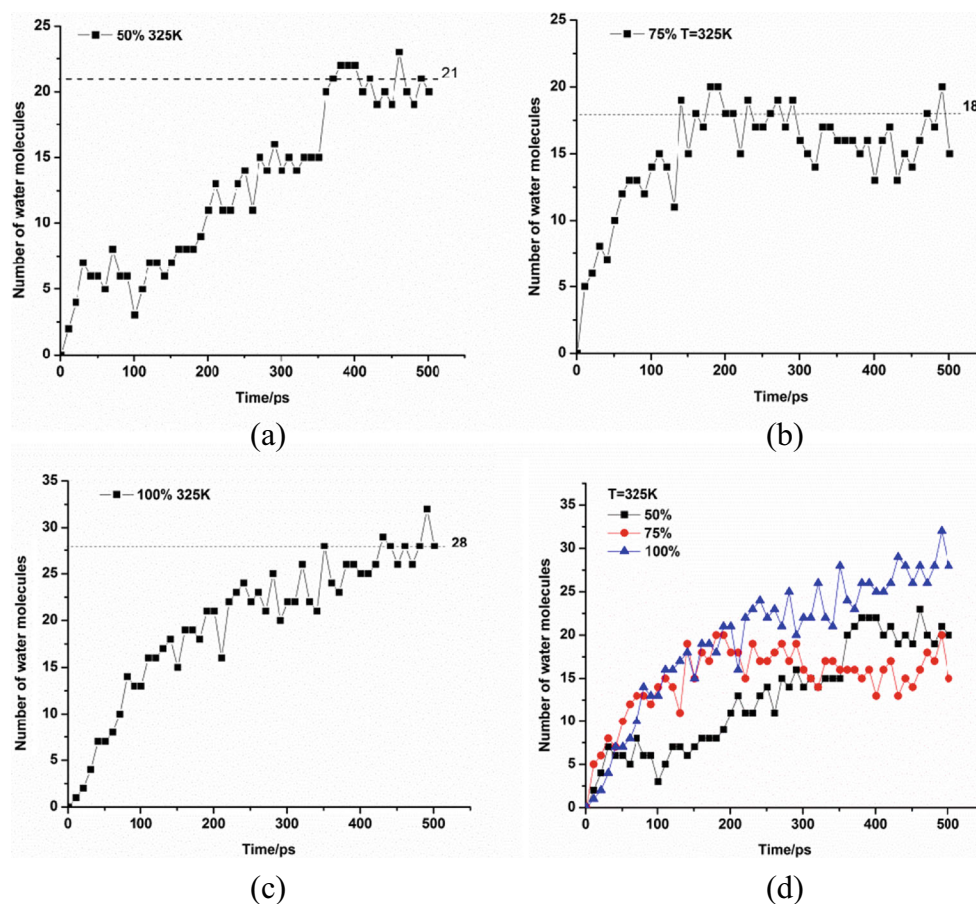
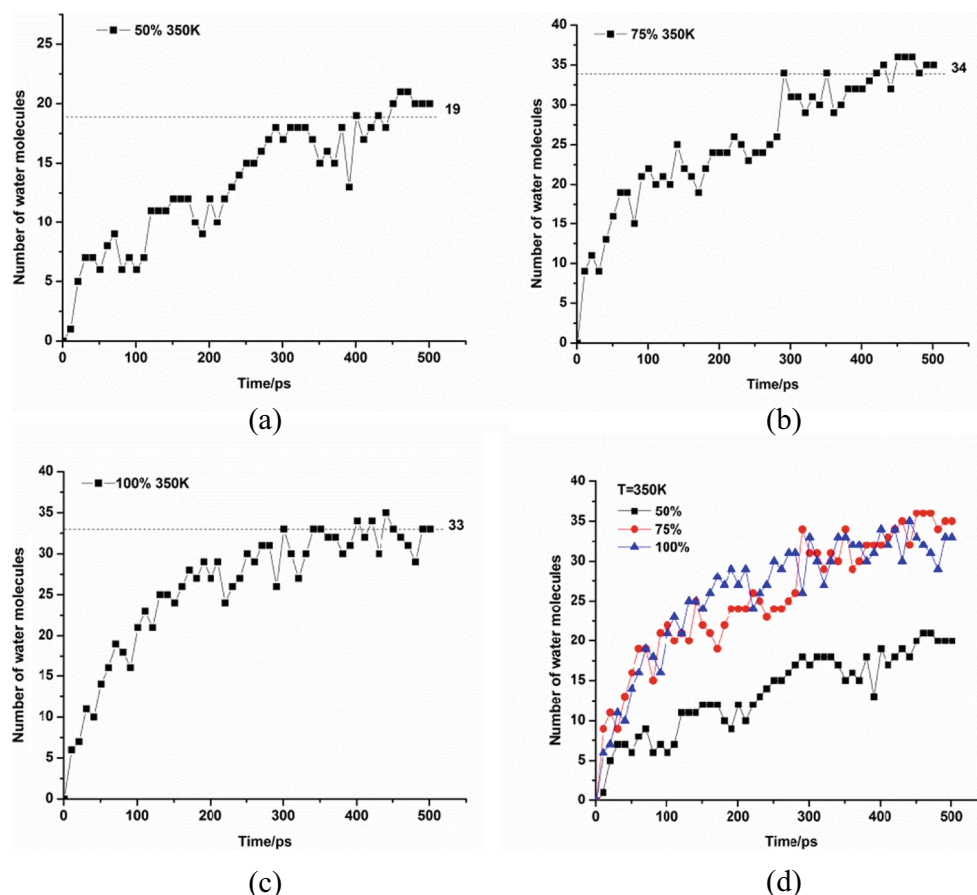


Fig. 8 Water absorption curves of hydrogel-water interface with different cross-linking degree at 350 K



we assume that the water absorbencies of the six hydrogel surfaces are almost the same. Thus, when the hydrogel is surrounded by water molecules, the number of water molecules entering the hydrogel during every 10 ps can be obtained from $N = N_i \times 6$. Similarly, the saturated water contents of the whole hydrogel can also be obtained from the water absorption curves.

Hydrogel model with saturated water contents

The water molecules are put into the initial structure of hydrogel shown in Fig. 2b with a random distribution to reach the saturated water contents. The number of water molecules is six times the number of saturated water molecules of one surface calculated in Hydrogel-water interface model section. The hydrogel with saturated water contents after geometry optimization is shown in Fig. 5a. Then a molecular dynamic simulation by using NPT ensemble is performed for 350 ps to ensure the structure swells freely. The volume expansion ratio of the hydrogel with saturated water contents is then

studied. The structure after the dynamic simulation is shown in Fig. 5b.

Results and discussion

Water absorbency of the hydrogel surface

Figure 6a-c shows the tendency of the number of water molecules in the hydrogel with different cross-linking degrees over time and at different temperatures. As shown in the figures, the number of water molecules in the hydrogel increases at the beginning, but tends to be gentle and fluctuates near a specific value, which means that the hydrogel has already been saturated after absorbing water from the hydrogel-water interface. The specific value is just the saturated water contents of the hydrogel-water interface.

From Figs. 6d, 7d, and 8d, it can be seen that before the hydrogel reaches saturation, the water absorption curves of hydrogel with 100 % and 75 % cross-linking degree are always higher than that with 50 % cross-

linking degree. In addition, the curves of hydrogel with 100 % cross-linking degree is just a little higher than that with 75 % cross-linking degree at the temperatures 325 K and 350 K (the curves shown in the figures are almost overlapped together). Therefore, it is concluded that a higher cross-linking degree results in a faster absorption of the water molecules in the hydrogel. However, this phenomenon will be unobvious at relatively high temperatures. It means that we can improve the water absorption rate through raising the cross-linking degree of PEGDGE/Jeffamine hydrogel at room temperature, but this phenomenon will be unobvious at relatively high temperatures.

From Figs. 6, 7, and 8a-c, it can also be obtained that the cross-linking degree has no obvious influence on the saturated water contents of the hydrogel surface. In other words, cross-linking degree does not affect the water absorbency of the hydrogel surface.

From Fig. 9a-c, it is easy to find that the influence of temperature on the saturated water contents of the hydrogel surface is not monotone increasing. For 100 % cross-link degree, the temperature has little influence on the water absorbency of the hydrogel surface.

Saturated water absorption content and volume expansion rate of saturated hydrogel

According to the assumption that the water absorbency of the six hydrogel surfaces are almost the same, the number of water molecules entering the hydrogel during every 10 ps can be calculated through $N = N_I \times 6$. Therefore, the water content can be obtained by $S = \frac{M_{H_2O}}{M_{Hydrogel}}$, in which M_{H_2O} is the mass of water molecules in the hydrogel and $M_{Hydrogel}$ is the mass of hydrogel without water.

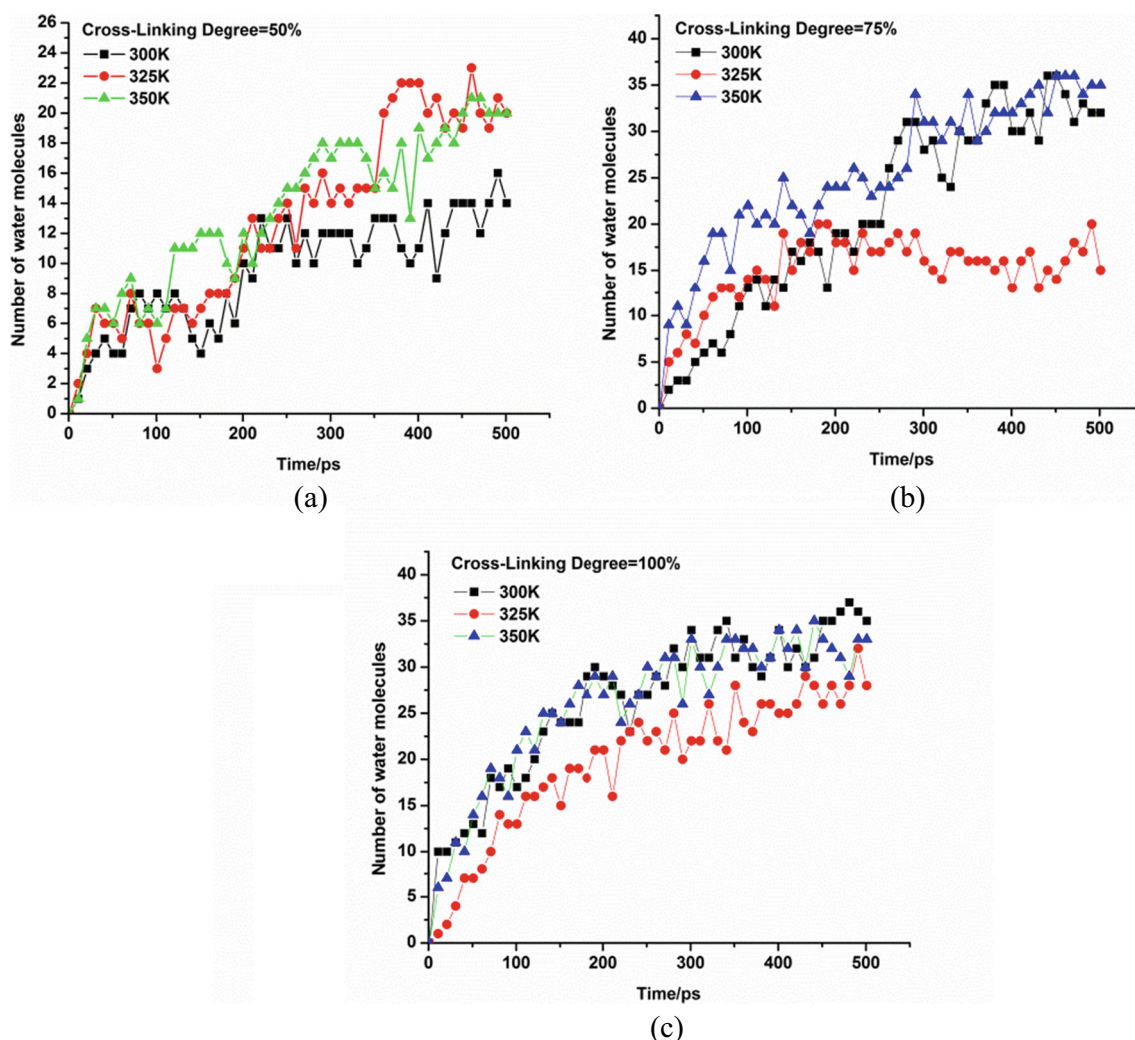


Fig. 9 Water absorption curves of hydrogel-water interface with the same cross-linking degree at different temperature

Similar to the phenomena shown in Figs. 6, 7, and 8, Figs. 10 and 11 show that water absorption curve rises at the beginning, but tends to be gentle and fluctuates near a specific value when the hydrogel comes to be saturated with water. In Table 1, the saturated water contents and volume expansion rates of the saturated hydrogel are listed. From Figs. 10, 11 and Table 1, it can be concluded that both the temperature and the cross-linking degree influence the saturated water content and the volume expansion rate of the saturated hydrogel, but the tendency is not monotonic. However, Fig. 11a shows that at the temperature 300 K and before the hydrogel reaches saturation, a higher cross-linking degree results in higher water absorption rate. However when the temperature rises to 325 K or 350 K, the water absorption curves of hydrogel with 100 % and 75 % cross-linking degrees are almost overlapped. As mentioned before, it means that the water absorption rate can be improved through raising the cross-linking degree of PEGDGE/Jeffamine

hydrogel at room temperature. However, the method cannot work at relatively high temperatures.

Conclusions

In this paper, the water absorbency of the hydrogel surface was studied by using the molecular dynamic simulation method. The saturated water content and the volume expansion rate of saturated hydrogel were also investigated. Several hydrogel-water interface models with different cross-linking degrees were built innovatively. The water absorption curves of the hydrogel-water interface and the whole hydrogel under different temperatures were compared. The simulation results show that the water absorption content of the hydrogel and its surface have saturation values. Both temperature and cross-linking degree of the hydrogel influence the saturated water absorption content of the hydrogel and

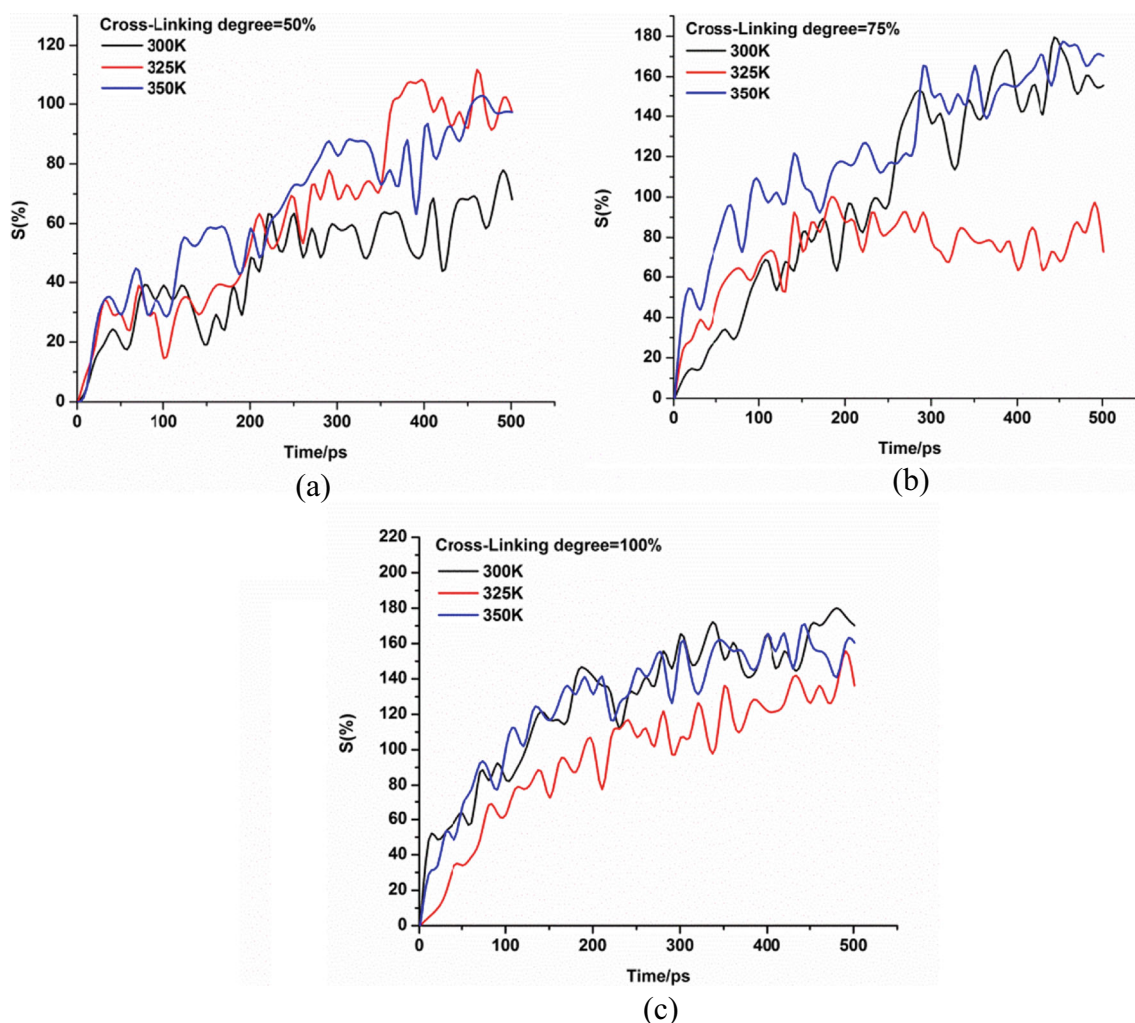


Fig. 10 Water absorption curve of hydrogel with the same cross-linking degree at different temperatures

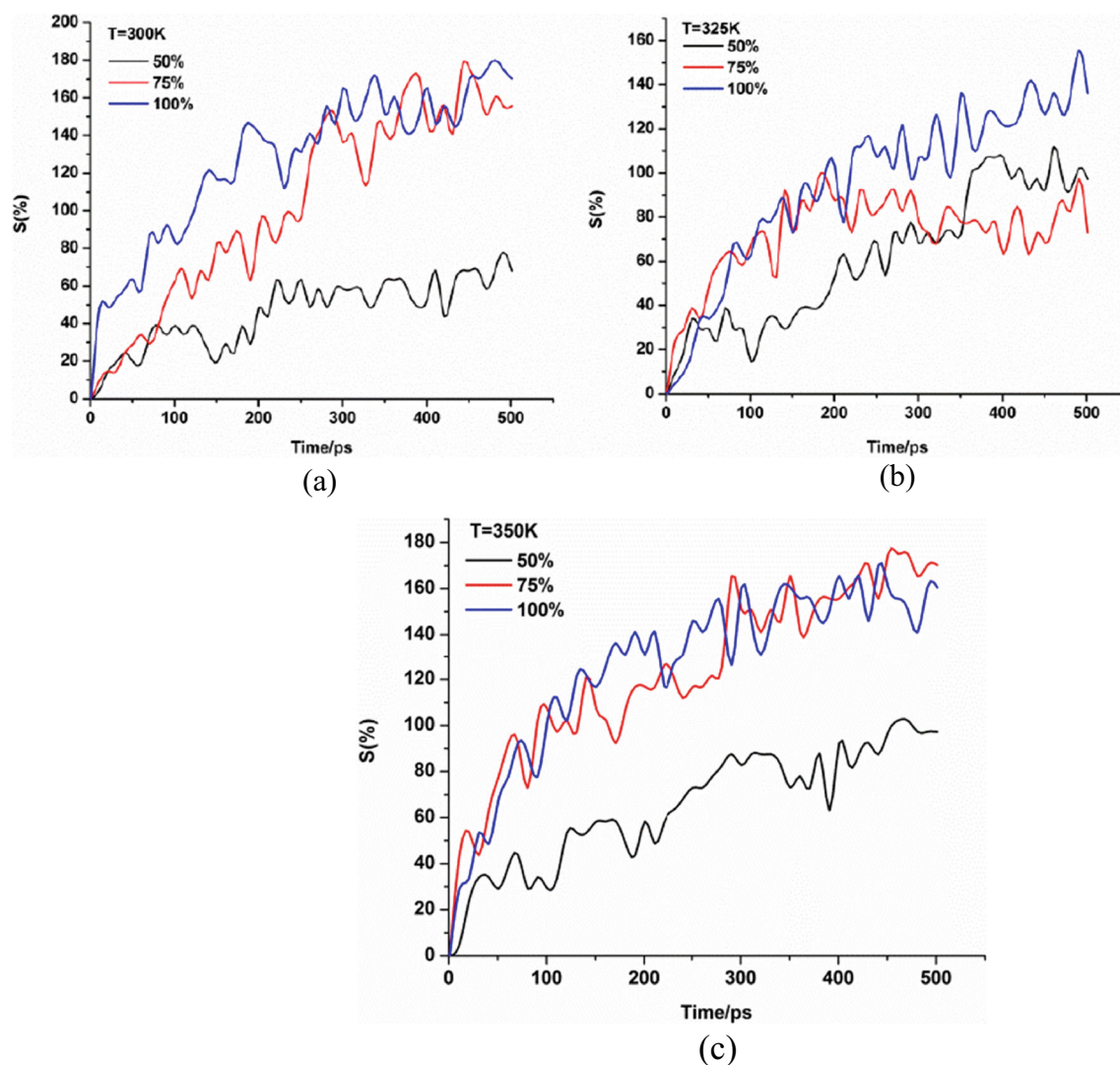


Fig. 11 Water absorption curves of hydrogel with different cross-linking degree at temperature 350 K

its surface, but the tendency is not monotonic. However, before the hydrogel attains saturation, the hydrogel with

higher cross-linking degree can absorb water faster. At high temperatures, this phenomenon becomes unclear.

Table 1 Volume expansion rate and saturated water content of hydrogel

Temperature	Cross-linking degree	Initial dimension	Final dimension	Volume expansion rate	Saturated water content
300 K	50 %	15 Å×15 Å×15 Å	18.75 Å×18.75 Å×18.75 Å	195.31 %	68.11 %
	75 %	15 Å×15 Å×15 Å	22.49 Å×22.49 Å×22.49 Å	337.05 %	160.54 %
	100 %	15 Å×15 Å×15 Å	22.86 Å×22.86 Å×22.86 Å	353.96 %	165.41 %
325 K	50 %	15 Å×15 Å×15 Å	20.65 Å×20.65 Å×20.65 Å	260.91 %	102.16 %
	75 %	15 Å×15 Å×15 Å	19.82 Å×19.82 Å×19.82 Å	132.13 %	87.57 %
	100 %	15 Å×15 Å×15 Å	22.03 Å×22.03 Å×22.03 Å	316.79 %	136.22 %
350 K	50 %	15 Å×15 Å×15 Å	24.13 Å×24.13 Å×24.13 Å	416.29 %	92.43 %
	75 %	15 Å×15 Å×15 Å	20.99 Å×20.99 Å×20.99 Å	274.01 %	165.41 %
	100 %	15 Å×15 Å×15 Å	22.63 Å×22.63 Å×22.63 Å	343.38 %	160.54 %

Also, both temperature and cross-linking degree influence the volume expansion rate of saturated hydrogel but the tendency is not monotonic.

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