Soft Matter

PAPER

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Cite this: DOI: 10.1039/c7sm01102d

Porous double network gels with high toughness, high stretchability and fast solvent-absorption

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Received 3rd June 2017,
Accepted 10th August 2017

DOI: 10.1039/c7sm01102d

rsc.li/soft-matter-journal

Using the freeze-drying method, we fabricated porous double network gels with high toughness, high stretchability and fast solvent-absorption. When the freezing temperature was −20 °C and the freezing time was 24 hours, pores with diameters around 300 μm could form in the gel. When the freezing temperature was lowered to −196 °C and the freezing time was reduced to 10 minutes, monodisperse pores with diameters around 15 μm could form in the gel. We found out that both porous gels fabricated under different conditions could absorb solvent much more and much faster than a nonporous gel. Furthermore, we found that the rupturing strain, stiffness and strength of the porous double network gels were all comparable to the nonporous double network gel when containing the same amount of solvent. The unique combination of the mechanical properties of the porous double network gels might motivate new explorations of gels in practical applications.

Introduction

When submerged in a solvent, a polymer network can swell and result in a gel. For the past decade, gels have been successfully engineered to exhibit customized properties and widely explored in diverse applications ranging from artificial muscles and biocompatible devices to ionic electrodes and soft robotics.[1] For example, Sun *et al.* have recently fabricated a highly stretchable and transparent actuator by coating ionic gel layers on the surface of a dielectric elastomer.[2,3] As another example, environmentally responsive gels have been extensively explored as self-regulating valves in microfluidic devices.[4] However, two well-known features of gels greatly limiting their practical applications are their generally poor mechanical properties and slow solvent absorption or swelling.

Different strategies have been adopted by researchers to address these two limitations. To improve the mechanical properties of gels including fracture toughness, strength and stretchability, polymer gels with different network topologies and crosslinkers have been synthesized. For instance, polymer gels with slide-rings as crosslinkers can stretch more than 10 times their original length.[5,6] Inorganic nanoparticles such as nanoclay and silica have also been explored as crosslinkers to enhance the strength of gels.[7–9] In addition, double network gels have been synthesized with remarkably high fracture toughness, stretchability and strength.[10] Those advancements in making strong, tough and highly stretchable gels have greatly motivated researchers to explore many innovative applications of gels. For instance, hydraulic actuators and robots have been fabricated using tough double network hydrogels.[11] Fire-resistant double network hydrogel-fabric laminates have also been proposed for life saving applications.[12]

The time for solvent absorption or swelling of gels is mainly determined by the solvent diffusion, which is often too slow for the applications of gels.[13] For example, double network gels have been explored for cooling buildings through solvent evaporation.[14] The solvent absorption rate of a gel is directly correlated with its water charging efficiency, which is critical for that specific application. To enhance the rate of solvent-absorption or swelling, porous gels have been fabricated through various techniques. Macroporous gels polymerized under reduced pressure show 10 times faster swelling rates than a nonporous gel.[15] Microporous gels have also been synthesized through the freeze-drying method, which also show much faster swelling or deswelling rates.[16] However, most previously synthesized porous gels are very brittle and weak because of the existence of a large number of defects (pores) in the gels.

In this article, we combined the two strategies discussed above to make porous double network gels with excellent mechanical properties, fast solvent-absorption or swelling, and higher solvent-absorption capacity. Double network gels usually have very high fracture toughness; their strength and stretchability are extremely defect-insensitive. As a result, porous double network gels fabricated in the current study have almost identical stretchability and strength to nonporous double network gels. Meanwhile, with the aid of capillary forces, porous double network gels have much faster solvent-absorption rates and higher solvent-absorption capacities than nonporous double network gels.

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Experimental section

Materials

Alginate was kindly provided by FMC BioPolymer, LF10/60, USA. Acrylamide (AAm) (99+%) was purchased from Acros, USA. *N*,*N*′-Methylene bis(acrylamide) (MBAA), ammonium persulfate (APS) (>98%), *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TEMED) (>99%), and calcium sulfate dihydrate (98%) were purchased from Sigma Aldrich. All materials were used as received without further treatment.

Synthesis of a double network hydrogel

A double network hydrogel was prepared based on the method described in the literature[10] with minor modifications.[17] 1 g of alginate and 8 g of acrylamide were dissolved in 51 g of deionized water, and then mixed with 0.0048 g of MBAA and 0.02 g of APS, which were the crosslinker and thermal initiator for acrylamide, respectively.

The mixture was stirred at room temperature for at least 2 hours until homogeneous. After that, the solution was degassed in a vacuum chamber and used as Solution 1; while 0.02 g of TEMED, the initiator accelerator, and 0.1328 g of calcium sulfate dehydrate, the ionic crosslinker for alginate, were dissolved in 5 g of deionized water, sonicated for 2 min, and used as Solution 2.

Solution 1 and Solution 2 were mixed fast and homogeneously, and then rapidly poured into a customized mould with dimensions of 50 mm × 20 mm × 20 mm or 50 mm × 20 mm × 40 mm. Finally, the specimen was transferred into an oven at 53 °C for 100 minutes, after which the polymerization of AAm was complete, and a double network hydrogel was formed.

Fabrication of dry porous double network polymers

The double network gel was removed from the mould after fabrication, and then frozen at −20 °C for 24 hours, or frozen under liquid nitrogen (−196 °C) for 10 minutes; after that, the frozen samples were transferred into a freeze-dryer (Labconco freeze-dry system) for complete lyophilization, and dry macroporous and microporous polymer matrices were generated.

Fabrication of a dry nonporous double network polymer

The double network tough gel was removed from the mould after fabrication, and then dried at room temperature for 1 week for complete dryness.

Characterization

Scanning electron microscopy. The morphologies of the surfaces of the dry polymers were observed using a FEI/Philips XL30 scanning electron microscope (SEM). The samples were coated with iridium using a sputter-coater (EMITECH K575X) for 7 s at 3×10^{-3} Mbar before SEM imaging.

Tensile tests. Tensile tests for the different hydrogels were conducted using an Instron Machine (5965 Dual Column Testing Systems, Instron) with a 1000 N loading cell. The samples were cut into dumbbell-shape. The ends of the samples were glued onto acrylic plates that were clipped by the clamps of the Instron Machine. The engineering strain rate for the tensile tests was fixed at 0.05 s^{-1}. For each condition, 3 measurements were carried out.

Measurements of the swelling kinetics of gels. Gels were immersed in DI water at room temperature. The gels were continuously retrieved from the DI water. The swelling ratios of the hydrogels were measured gravimetrically as a function of time after wiping off excess water on the surface of the gels with dry paper (Kimwipes Delicate Task Kimtech Science Wipers). The swelling ratio is defined as W_t/W_o, where W_t is the weight of the swollen gel, and W_o is the initial weight of the dry polymer.

Results and discussion

Microstructures of the double network gels

We first studied the microstructures of the porous double network gels fabricated under different conditions as discussed in the Experimental section. Fig. 1(A-1)–(A-3) show macroscopic photos of the fabricated double network polymers. Fig. 1(B-1)–(B-3) show the SEM images of the porous and nonporous structures of the double network polymers. In particular, Fig. 1(A-1) and (B-1) show the macroporous double network polymer fabricated by freezing the gel at −20 °C for 24 hours prior to lyophilization, Fig. 1(A-2) and (B-2) show the microporous double network polymer fabricated by freezing the gel at −196 °C for 10 minutes prior to lyophilization, and Fig. 1(A-3) and (B-3) show the nonporous double network polymer fabricated by air-drying the gel at room temperature for 1 week. It can be seen that the porous structures were successfully generated in the double network polymers through the freeze-drying process. The size of the pore in the double network polymer in Fig. 1(B-1) is roughly 300 μm, which is significantly larger than the pore size shown in Fig. 1(B-2), which is around 15 μm. In this article, the double network polymer with a pore size of 300 μm is referred to

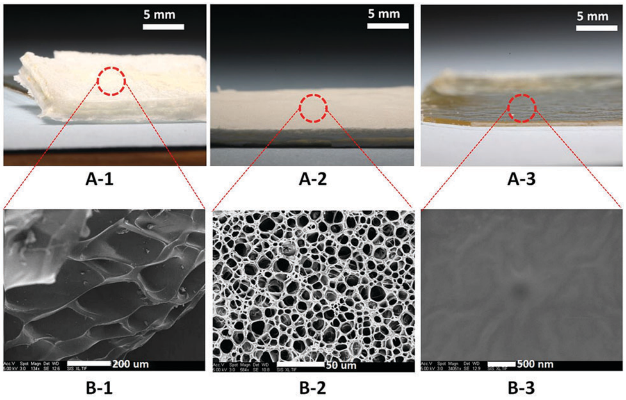

Fig. 1 Photographs of double network polymers with different microstructures: (A-1) macroporous double network polymer, (A-2) microporous double network polymer, and (A-3) nonporous double network polymer. SEM images of the surfaces of the double network polymers with different microstructures: (B-1) macroporous double network polymer, (B-2) microporous double network polymer, and (B-3) nonporous double network polymer.

as a macroporous polymer/gel and the polymer with a pore size of 15 μm is referred to as a microporous polymer/gel.

We next estimated the porosities of both macroporous and microporous double network polymers. The densities of the fabricated double network polymers can be estimated based on the measurements of their weights and volumes. In our experiments, in the dry state, the macroporous polymer has a density of around 0.2 g cm^{-3}, the microporous polymer has a density of around 0.26 g cm^{-3}, and the nonporous polymer has a density of around 0.73 g cm^{-3}. Assuming that the solid skeletons of the porous polymers have the same density as that of the nonporous polymer, we can further estimate the porosities (defined as the volume ratio of pores) for both the macroporous gel and microporous gel to be 73% and 64%, respectively.

When the gel was frozen at a temperature below 0 °C, the water inside the gel transformed into ice crystals. Through lyophilization, the ice crystals directly turned into vapour, and the spaces occupied by ice became pores left in the gel. When the frozen temperature was −196 °C, the water transformed into ice crystals immediately and the crystals had no time to grow to bigger sizes. Therefore, the pores in the gel are small as shown in Fig. 1(B-2). When the frozen temperature was −20 °C, the water inside the gel slowly turned into ice crystals, which had more time to grow bigger and hence introduced significantly bigger pores into the gel as shown in Fig. 1(B-1). As a result, we can conclude that by tuning the freezing temperature, pores of different sizes could be easily introduced into double network gels. The lower the frozen temperature is, the smaller the pore size will be.

Solvent absorption kinetics of the double network gels

We next investigated the solvent absorption kinetics of the double network gels prepared under different conditions as described above.

In the first experiment, dry macroporous, microporous and nonporous double network polymers with the same thickness of about 2 mm were submerged in DI water. The polymers were continuously retrieved from the DI water at different times, and their weights were measured after wiping off excess water from their surfaces. After the gels were saturated with water, they were air dried completely and then put into water to re-swell for another round of water absorption kinetics test, from dry polymers to fully swollen gels.

Fig. 2(A) plots the swelling ratios of the gels as functions of time for the first and second rounds of water absorption experiments. For the first round of test, we can observe that water absorption rates in both the macroporous gel and microporous gel were dramatically higher than that of the nonporous gel. In addition, the macroporous gel absorbed water slightly faster than the microporous gel. For example, to reach a swelling ratio equal to 5, the macroporous polymer took less than 27 minutes and the microporous polymer needed about 40 minutes; however, the nonporous polymer needed almost 120 minutes. Based on the measurements, we can also estimate the diffusivities of both porous and nonporous gels. We define the time needed for a gel to absorb solvent 15 times that of its initial weight as the characteristic time: t. The diffusivity D of the gels can be estimated by $D \sim H^2/t$, where H is the thickness of the gels. Using the data shown in Fig. 2(A), we calculated the diffusivity of the nonporous gel to be around 10^{-10} m^2 s^{-1}, and the diffusivities for both the macroporous gel and microporous gel are around 3×10^{-10} m^2 s^{-1}.

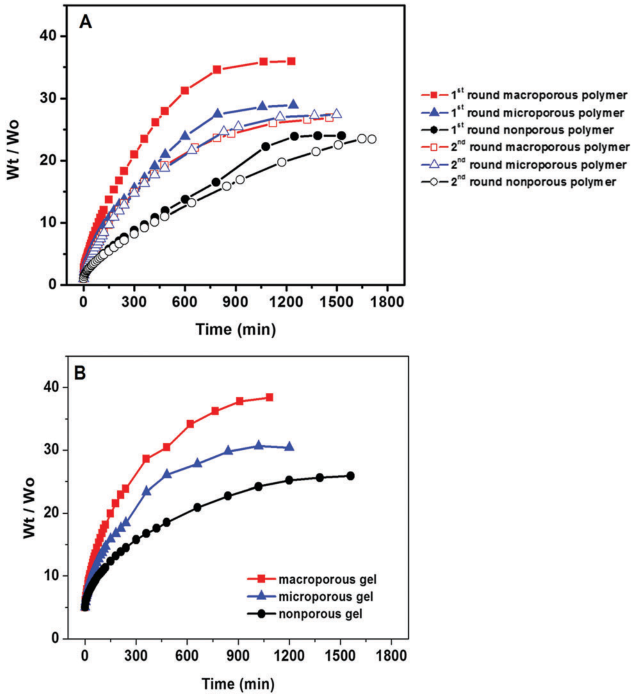

Fig. 2 Water absorption kinetics of double network gels. (A) All polymers went through water absorption tests for two rounds, from dry states to saturated states. In the first round, all polymers started to absorb water from dry states until they became saturated, and then they were air dried completely; after that, all polymers started to absorb water for the second round from dry states until they became saturated: (–■–) macroporous polymer water absorption for the first round and (–□–) macroporous polymer water absorption for the second round; (–▲–) microporous polymer water absorption for the first round and (–△–) microporous polymer water absorption for the second round; and (–●–) nonporous polymer water absorption for the first round and (–○–) nonporous polymer water absorption for the second round. (B) All gels absorbed water from the wet state (initially, all polymers contain 4 times their own weight of water) until they became saturated: (–■–) macroporous tough polymer, (–▲–) microporous tough polymer, and (–●–) nonporous tough polymer.

Another observation we found is that the porous gels have higher water absorption capacity than the nonporous gel. To be more specific, in the equilibrium state, the macroporous gel can absorb roughly 50% more water than the nonporous gel with the same weight, and the microporous gel can absorb roughly 17% more water than the nonporous gel.

Fig. 2(A) also shows that in the re-swelling test, both macroporous and microporous gels still showed higher water absorption rates than the nonporous one, though the water absorption in the macroporous gel is slightly slower during the re-swelling test. We think that it is probably due to the partial collapse of the pores in macroporous gel during the air-drying process after its first round swelling test.

In many applications, gels often stay in wet or partially swollen states. To study the water absorption kinetics in partially swollen gels, we first let both porous and nonporous dry polymers of the same thickness to absorb water as much as four times that of their weights. After that, we put the gels in well-sealed Petri dishes for a couple of hours without contacting water to homogenize the interior solvent distribution. We then measured the water absorption kinetics as we did in the previous experiments. The results are shown in Fig. 2(B). We could clearly see that starting from wet states, the porous gels also demonstrated faster water absorption rates than the nonporous one, with the macroporous gel slightly faster than the microporous gel.

Another simple and clear demonstration of the water absorption kinetics of various double network polymers is shown in Fig. 3. One drop of dyed water was dripped from the pipette onto the surface of a dry macroporous polymer, a dry microporous polymer, and a dry nonporous polymer. The absorption rate of the water droplet into each dry polymer was quite different, as shown in Fig. 3(A)–(C). The dyed water droplet migrated into the macroporous polymer in a very short time; the entire water droplet was absorbed by the polymer within only 40 seconds. On the other hand, the water droplet was completely absorbed by the microporous polymer in 15 minutes. The water droplet on the top of the nonporous polymer, however, migrated into the polymer completely after 60 minutes.

Based on these observations in Fig. 2 and 3, we can conclude that the porous structures in the tough polymers exceedingly accelerate the liquid migrations or the molecule exchanges, and greatly increase the swelling ratios of the gels. These improved properties endow the porous double network polymers with great potential to be superabsorbent hydrogels,[18,19] which have a wide range of applications in personal care products, such as contact lenses[20] and baby or disposable diapers;[21–23] in the biomedical area,[24] for example, as antibacterial materials[25] and wound dressings,[26] in tissue engineering,[27] and as biosensors;[28] and in agricultural practices, such as water management in soil.[29]

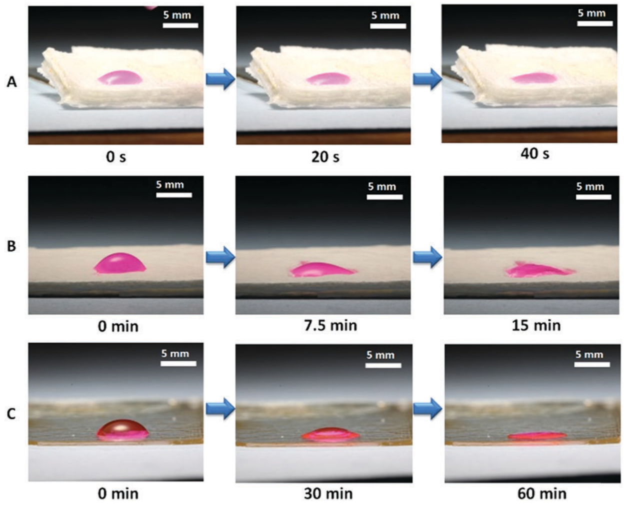

Fig. 3 Demonstration of water absorption processes of macroporous, microporous and nonporous double network polymers. One drop of dyed water was dripped from the pipette onto the surface of a (A) dry macroporous polymer, (B) dry microporous polymer, and (C) dry nonporous polymer. Solvent absorption processes of the droplets by the polymers were recorded using a digital camera. (A) A dyed water droplet completely migrated from the surface into the macroporous polymer within about 40 seconds. (B) A dyed water droplet completely migrated from the surface into the microporous polymer within about 15 minutes. (C) A dyed water droplet completely migrated from the surface into the nonporous polymer within about 60 minutes.

The observed dramatic differences of solvent absorption by the porous and nonporous double network gels can be easily understood by considering their microstructures. For a nonporous gel, solvent migrates into it mainly through diffusion, and the corresponding effective diffusivity is relatively low. For instance, the diffusion coefficient in a contact lens gel is around 10^{-7} cm^2 s^{-1}.[30] By introducing pores into a double network gel, solvent can be absorbed by the gel with the additional help of capillarity, just like solvent absorbed by a sponge. Such a capillarity-driven solvent flux is usually called Darcy's flow,[31] which can be much faster than the diffusion process. Therefore, as shown in Fig. 2, the solvent absorption in a porous gel was significantly faster than a nonporous one. The internal pores also directly led to high absorption capability of the porous double network gel. In addition to the gel skeleton, the internal pores in the polymer can also encapsulate a certain amount of solvent.

Mechanical properties of the double network gels

As mentioned in the Introduction, porous gels usually have poorer mechanical properties than nonporous gels.[32] To make porous gels useful in many applications, their mechanical properties such as strength and stretchability need to be greatly improved in general.

We then studied the mechanical behaviors of double network gels with different microstructures fabricated by us. In the experiments, we first let the gels absorb a certain amount of water. After that, we put the gels in well-sealed Petri dishes for a couple of hours without contacting water to homogenize the interior solvent distribution. The stress *vs.* stretch relationships of the gels with four different swelling ratios were measured through simple extension tests. For each condition, the experiments were conducted three times. One representative curve for each condition was selected and is plotted in Fig. 4. For all four different swelling ratios, stress *vs.* stretch curves for the nonporous, microporous and macroporous gels are surprisingly similar, considering the porosities of the macroporous gel and microporous gel are as high as about 70%. We believe such results are mainly due to the high toughness of the double network gels. Although the pores in the microporous gel and macroporous gel can be regarded as defects, the stretchabilities of the porous gels are comparable to that of the nonporous gel, which is simply because the double network gel is not sensitive to the defect of such small size. In particular, a recent study has shown that the double network gel becomes flaw sensitive when the flaw size is bigger than roughly 1 mm.[33] Considering the pore sizes in both macroporous and microporous gels fabricated in our study are less than 500 μm, we can understand why the porous double network gels have almost identical rupturing stretch to the nonporous gel as shown in Fig. 4(A–D).

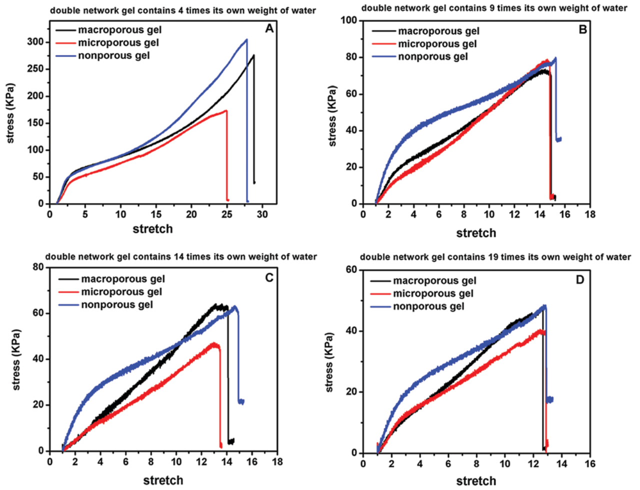

Fig. 4 Stress *vs.* stretch curves for various double network gels under simple extension tests. (A) Stress *vs.* stretch curves for gels containing 4 times their own weight of water; (B) stress *vs.* stretch curves for gels containing 9 times their own weight of water; (C) stress *vs.* stretch curves for gels containing 14 times their own weight of water; and (D) stress *vs.* stretch curves for gels containing 19 times their own weight of water. In all the plots, black curves indicate macroporous gels, red curves indicate microporous gels, and blue curves indicate nonporous gels.

From Fig. 4(A–D), we also found that the porous double network gels have comparable stiffnesses and strengths to the nonporous gel. This result is even more unexpected. When examining the surfaces of the porous gels, we can see that most spaces are occupied by the pores as shown in Fig. 1(B-1) and (B-2), and those pores, even after being filled with water, provide negligible contribution to the overall strength and stiffness to the gels. We believe that such a result is mainly due to the effects of swelling on the mechanical properties of the gels. With the increase of the swelling ratio, both the stiffness and strength of a nonporous gel decrease as shown in Fig. 4(A–D). Because of the high porosities of both the macroporous gel and microporous gel, with the same swelling ratio, the solid skeletons of the porous gels actually swell less than that of the nonporous gel. Consequently, with the same swelling ratio, the solid skeletons of the porous gels should be both stiffer and stronger than the nonporous gel, which compensates for the weakening/softening effects of internal pores. As the result, the overall stiffness and strength of the porous gels become comparable to those of the nonporous gel. Although we have not conducted any fracture tests of both porous and nonporous double network gels, we expect that the fracture toughness of the nonporous, microporous and macroporous double network gels fabricated in the current study should also be very close to each other.

Concluding remarks

In this study, we have fabricated highly porous double network tough gels through the freeze-drying method. By varying the freezing temperature and time, the size of the pores in the gels can be adjusted from 300 μm to 15 μm. By introducing pores into the double network gels, we found that the fabricated porous gels have great advantages over the nonporous gel; they can absorb much more solvents with significantly faster rates with the extra help of capillarity, just like solvent absorbed by a sponge.

Another interesting finding is that, because of the high toughness of double network gels, the stretchabilities of the fabricated porous gels were comparable to that of the nonporous gel, despite the existence of a large number of defects (pores). We also found that for a fixed swelling ratio, the strength and stiffness of the porous double network gels fabricated by us were comparable to those of the nonporous gel. In summary, we successfully fabricated porous double network gels with much-improved solvent absorption rates and solvent absorption capability without sacrificing their mechanical properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

S. Cai acknowledges the support from the American Chemical Society through an award [grant number 55379-DNI9].

Notes and references

1 Y. S. Zhang and A. Khademhosseini, *Science*, 2017, **356**, eaaf3627.
2 C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides and Z. Suo, *Science*, 2013, **341**, 984–987.
3 J. Y. Sun, C. Keplinger, G. M. Whitesides and Z. Suo, *Adv. Mater.*, 2014, **26**, 7608–7614.
4 D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss and B.-H. Jo, *Nature*, 2000, **404**, 588–590.
5 Y. Okumura and K. Ito, *Adv. Mater.*, 2001, **13**, 485–487.
6 A. B. Imran, K. Esaki, H. Gotoh, T. Seki, K. Ito, Y. Sakai and Y. Takeoka, *Nat. Commun.*, 2014, **5**, 5124.
7 K. Haraguchi and T. Takehisa, *Adv. Mater.*, 2002, **14**, 1120–1123.
8 Q. Wang and Z. Gao, *J. Mech. Phys. Solids*, 2016, **94**, 127–147.
9 K. Haraguchi and H.-J. Li, *Macromolecules*, 2006, **39**, 1898–1905.
10 J.-Y. Sun, X. Zhao, W. R. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. Suo, *Nature*, 2012, **489**, 133–136.
11 H. Yuk, S. Lin, C. Ma, M. Takaffoli, N. X. Fang and X. Zhao, *Nat. Commun.*, 2017, **8**, 14230.
12 W. R. Illeperuma, P. Rothemund, Z. Suo and J. J. Vlassak, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2071–2077.
13 P. Calvert, *Adv. Mater.*, 2009, **21**, 743–756.
14 S. Cui, C. Ahn, M. C. Wingert, D. Leung, S. Cai and R. Chen, *Appl. Energy*, 2016, **168**, 332–339.

15 X.-Z. Zhang, F.-J. Wang and C.-C. Chu, *J. Mater. Sci.: Mater. Med.*, 2003, **14**, 451–455.

16 X. Zhao, J. Kim, C. A. Cezar, N. Huebsch, K. Lee, K. Bouhadir and D. J. Mooney, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 67–72.

17 Q. He, Z. Wang, Y. Yan, J. Zheng and S. Cai, *Extreme Mech. Lett.*, 2016, **9**, 165–170.

18 F. Ullah, M. B. H. Othman, F. Javed, Z. Ahmad and H. M. Akil, *Mater. Sci. Eng., C*, 2015, **57**, 414–433.

19 C. Chang, B. Duan, J. Cai and L. Zhang, *Eur. Polym. J.*, 2010, **46**, 92–100.

20 H. A. Ketelson, D. L. Meadows and R. P. Stone, *Colloids Surf., B*, 2005, **40**, 1–9.

21 F. L. Buchholz and A. T. Graham, *Modern superabsorbent polymer technology*, Wiley-VCH, New York, 1998, pp. 1–152.

22 L. Brannon-Peppas and R. S. Harland, *Absorbent polymer technology*, Elsevier, Amsterdam, 1990, ch. 1–4.

23 W. Dohrn, R. Buettner, I. Notz, G. Werner, C. Knobelsdorf, E. Herrmann and M. Schuemann, *US Pat.*, 7052775, 2006.

24 E. Caló and V. V. Khutoryanskiy, *Eur. Polym. J.*, 2015, **65**, 252–267.

25 P. K. Murthy, Y. M. Mohan, K. Varaprasad, B. Sreedhar and K. M. Raju, *J. Colloid Interface Sci.*, 2008, **318**, 217–224.

26 P. H. Corkhill, C. J. Hamilton and B. J. Tighe, *Biomaterials*, 1989, **10**, 3–10.

27 J. Kim, K.-W. Lee, T. E. Hefferan, B. L. Currier, M. J. Yaszemski and L. Lu, *Biomacromolecules*, 2007, **9**, 149–157.

28 A. Pourjavadi, H. Ghasemzadeh and R. Soleyman, *J. Appl. Polym. Sci.*, 2007, **105**, 2631–2639.

29 S. M. Ibrahim, K. M. El Salmawi and A. Zahran, *J. Appl. Polym. Sci.*, 2007, **104**, 2003–2008.

30 F. Fornasiero, F. Krull, J. M. Prausnitz and C. J. Radke, *Biomaterials*, 2005, **26**, 5704–5716.

31 S. Whitaker, *Transp. Porous Media*, 1986, **1**, 3–25.

32 L. J. Gibson and M. F. Ashby, *Cellular Solids*, Cambridge Univ Press, Cambridge, 1997.

33 C. Chen, Z. Wang and Z. Suo, *Extreme Mech. Lett.*, 2017, **10**, 50–57.