

A Mechanically Strong Conductive Hydrogel Reinforced by Diaminotriazine Hydrogen Bonding*

Qian Wu^a, Bing Xu^a, Jun-jie Wei^b, Qing Wang^a, Qi-gang Wang^b and Wen-guang Liu^{a**}

^a*School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300350, China*

^b*School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China*

Abstract Over the past decades, the urgent need for high strength conductive hydrogels in diverse applications has motivated an unremitting effort to combine the improved mechanical properties of hydrogels with conductive performances. In this work, high strength conductive hydrogels intensified with intermolecular hydrogen bonding are fabricated by *in situ* mixing poly(2-vinyl-4,6-diamino-1,3,5-triazine-co-polyethylene glycol diacrylates) (PVDT-PEGDA) hydrogels with poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS). The conductive hydrogels in deionized water exhibit high mechanical performances with compressive strength and tensile strength in the range of 7.58–9.52 MPa and 0.48–1.20 MPa respectively, which are ascribed to the intermolecular hydrogen bonding interactions of diaminotriazine-diaminotriazine (DAT-DAT) in the network. Meanwhile, adding PEDOT/PSS can significantly increase both the specific conductivities and equilibrium water contents of the hydrogels. These cytocompatible conductive hydrogels may have a great potential to be used as electrical stimuli responsive soft biomaterials.

Keywords Conductive hydrogels; High strength; PEDOT/PSS; Hydrogen bonding

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1960-3>.

INTRODUCTION

Electrically conductive hydrogels, as a kind of intelligent and versatile polymeric composites, have received sufficient attention due to the combination of highly hydrated cross-linked hydrogels with inherently conductive electroactive polymers in the past few years^[1–3]. The conductive hydrogels with easy-to-tailor properties show a wide range of applications, including supercapacitors, electrodes, fuel cells, actuators, rechargeable lithium batteries, scaffolds for tissue engineering and biomedical sensors^[4–10]. However, one of the most obvious and intractable drawbacks of conductive hydrogels is the lack of sufficient mechanical strength, which seriously limits the scope of their applications^[11, 12].

To date, most intensive studies for conductive hydrogels have focused on the improvement of their mechanical strength, such as the composite conductive hydrogels and double network conductive hydrogels^[13–19]. The conductive nanomaterials, including supramolecular nanofibers^[13], carbon nanotubes^[14], graphene^[15], and graphene oxide are used to blend into the hydrogel networks^[16] for preparing the composite

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51325305, 51473117 and 21274105) and National Key Research and Development Program (No. 2016YFC1101301).

** Corresponding author: Wen-guang Liu (刘文广), E-mail: wgliu@tju.edu.cn

Invited paper for special issue of “Hydrogel”

Received March 21, 2017; Revised April 7, 2017; Accepted April 11, 2017

doi: 10.1007/s10118-017-1960-3

conductive hydrogels. Alternatively, high strength conductive hydrogels can also be fabricated by the oxidative polymerization of conductive monomers, *e.g.* pyrrole and aniline inside the mechanically double network hydrogel matrices^[17–19]. However, these two methods involve rather complicated processes^[20]. Moreover, the low solubility of conductive polymers usually results in the difficulties in processing, and the heterogeneous and discontinuous distribution of conductive components in the hydrogel matrices^[17, 21].

In our previous work^[22, 23], we have reported the high strength hydrogels achieved by the interaction of intermolecular hydrogen bonding of diaminotriazine (DAT) residues or CN-CN dipole-dipole interactions in polyacrylonitrile (PAN). These hydrogen bonding or dipole-dipole reinforced hydrogels were prepared by one-step copolymerization of acrylonitrile or 2-vinyl-4,6-diamino-1,3,5-triazine (VDT) with hydrophilic monomers as well as a crosslinker. It is of importance to introduce the hydrophilic monomers into polymer chains for offsetting the hydrophobicity of DAT or PAN^[24, 25]. In this study, we aim at employing the backbone of hydrogen bonding-strengthened hydrogels prepared from 2-vinyl-4,6-diamino-1,3,5-triazine and polyethylene glycol diacrylates (PEGDA) to develop high strength conductive hydrogels.

It is well known that poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS) has water-dispersibility, good conductivity, prominent chemical (environmental) stability, and excellent biocompatibility^[26–28]. Thus, it is a convenient and facile approach to directly incorporate aqueous dispersion of PEDOT/PSS into the solution of VDT and PEGDA before the polymerization. It is anticipated that PEDOT/PSS can be dispersed uniformly and homogeneously in the solution of VDT and PEGDA, and also may endow hydrogels with electrical property. It is expected that the designed high strength conductive hydrogels have a great potential as electrical materials, biosensors and soft tissue engineering scaffolds.

EXPERIMENTAL

Materials

2-Vinyl-4,6-diamino-1,3,5-triazine (VDT) and acryloyl chloride (purity > 98%) were purchased from Tokyo Kasei Kogyo Company in Japan. Poly(ethylene glycol) (PEG, $M_w = 4000$, Sigma-Aldrich) was dried in a vacuum oven at room temperature for 24 h prior to use. Poly(ethylene glycol) diacrylate was synthesized according to the previously reported method^[23]. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT/PSS, 1.3 wt% dispersion in H₂O) was supplied by Tianjin Heowns Biochem LLC. Benzoyl peroxide (BPO, purity > 98%) and *N,N*-dimethylaniline (DMA) were obtained from Aladdin Biochemical Polytron Technologies Inc in Shanghai. All other chemicals and solvents were of analytical grade.

Preparation of Hydrogels

Poly(PEGDA-*co*-VDT) hydrogel and poly(PEGDA-*co*-VDT) with different volume contents of PEDOT/PSS hybrid gels were prepared according to the formulations shown in Table S1 (in the supporting information, SI). In this experiment, the mass ratio of monomer VDT and crosslinker PEGDA ($M_w = 4000$) was fixed at 2, and the mixture was dissolved in dimethyl sulfoxide (DMSO) to form a transparent monomer solution. The concentrations of VDT and PEGDA were set at 20 wt%. A specific volume of PEDOT/PSS was then added into the solution and vortexed vigorously to form a homogeneous mixture. Obviously, the transparent solution became a deep blue color after the addition of PEDOT/PSS, especially when more conductive components were added. Next, 3 wt% of BPO (relative to the total mass of VDT and PEGDA) was added into the solution and stirred thoroughly under nitrogen atmosphere, and the solution was placed into an ice bath for about 5 min. Subsequently, 3 wt% of DMA (relative to the total mass of VDT and PEGDA) was also added into the solution. After homogenization, the cooled mixture was quickly injected into the plastic rectangle molds (length 70 mm, width 50 mm) with a rubber gasket (thickness 0.5 mm) or the plastic cylinder-shaped molds, and kept at room temperature for 24 h. Finally, the prepared hydrogels were demolded and immersed into deionizer water that changed by fresh water every 12 h for 3 days to remove the impurities, including residual monomer and the solvent of DMSO at room temperature. The resultant conductive hydrogels were named as PVDT-PEGDA-*X*, where *X* indicates the concentration of PEDOT/PSS (in vol% of the dissolved mixture).

ATR-FTIR and Raman Spectroscopy

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Perkin Elmer Spectrum 100, USA) was applied to confirm the successful polymerization of VDT and PEGDA for the fabrication of PVDT-PEGDA-*X* hydrogels.

Raman spectroscopy was employed to confirm the successful incorporation of PEDOT/PSS as the conductive component in hydrogels. The spectra were recorded on a ThermoFisher DXR Raman Microscope with an excitation wavelength of 532 nm in dynamic mode from 0 cm⁻¹ to 3200 cm⁻¹ at a resolution of 1 cm⁻¹.

Mechanical Measurement

The mechanical properties of PVDT-PEGDA-*X* hydrogels were measured on a WDW-05 electromechanical tester (Time Group Inc, China) at room temperature. In this study, all the hydrogels were immersed in deionized water to reach swelling equilibrium before test. At least three specimens were tested for each measurement. For tensile tests, the hydrogels were cut into dumbbell-shaped samples in accordance with GBT 528-20094 (width: 2 mm, gauge length: 10 mm, thickness: 0.5 mm) using a customized cutter (Xuan Yu Inc, China). The rate of extension was fixed at 50 mm·min⁻¹. Besides, the cylindrical hydrogels (4 mm in height and 4 mm in diameter) were used for the compression tests and measured by the same tester at the fixed rate of 10 mm·min⁻¹. It is noted that all of the stresses measured are engineering stresses (σ), which are calculated according to the following formula (1):

$$\sigma = \frac{F}{A_0} \quad (1)$$

where F is the applied load and A_0 is the starting cross-sectional area.

Measurement of Hydrogel Conductivity

The hydrogel samples with definite shapes (10.0 mm in diameter, 1.0 mm in thickness) were sandwiched between two stainless steel plate electrodes to form a two-electrode system. All the specimens were immersed in deionized water for at least 3 days before test. The conductivities of different samples were determined from impedance spectra based on AC impedance method measured by a Metrohm Autolab PGSTA302N potentiostats-galvanostats (Netherlands) coupled with a computer. And the data were treated by Zview software. The conductivities (σ) are calculated by the following Eq. (2)^[29]:

$$\sigma = \frac{1}{R} \frac{d}{S} \quad (2)$$

where R is the resistance; d and S are the thickness and area of specimens, respectively.

Cytotoxicity Assay

The cytotoxicity of conductive hydrogels was tested using mouse fibroblast cells (L929, obtained from Runtai technology and development Co. Ltd, Tianjin). Mouse fibroblast cells were seeded in a 96-well plate coated with hydrogels and incubated for 48 h to evaluate the cytotoxicity of different hydrogel samples by the MTT assay. The culture medium was replaced with 400 μ L of fresh medium containing 40 μ L of MTT (3-(4,5-dimethyl-2-thia-zoyl)-2,5-diphenyl tetrazolium bromide, 5 mg·mL⁻¹ in PBS), and the cells were incubated for another 4 h. Finally, the whole medium was replaced with 300 μ L of DMSO per well to dissolve the formed crystals, and the plate was gently shaken for 15 min on an oscillator. The absorbance (Abs) of each well was measured at 490 nm on a Σ 960 plate-reader (Synergy HT, Biotek Company, US) with pure DMSO as a blank. The non-treated cells in Dulbecco's modified Eagle's medium (DMEM) were used as a control and the relative cell viability (RCV, mean $\pm$ SD, $n = 3$) was expressed as Eq. (3):

$$\text{RCV} = \frac{\text{Abs}_s}{\text{Abs}_c} \times 100\% \quad (3)$$

where Abs_s and Abs_c are the absorbance of the sample and control group, respectively.

RESULTS AND DISCUSSION

Characterization of the Conductive Hydrogels

In our previous studies^[23], we have demonstrated that high strength hydrogels could be synthesized by copolymerization of VDT and PEGDA, where diaminotriazine-diaminotriazine hydrogen bonding interaction greatly enhances the mechanical strengths of the obtained gels. Figure 1 displays the molecular structure of PVDT-PEGDA hydrogel and the network structure of PVDT-PEGDA-*X* hydrogel mixed with PEDOT/PSS. In our case, we found that the clear solutions containing 20 wt% of PVDT-PEGDA-*X* could form stable polymer hydrogels due to the combination of multiple hydrogen bonding and chemical crosslinking, as shown in

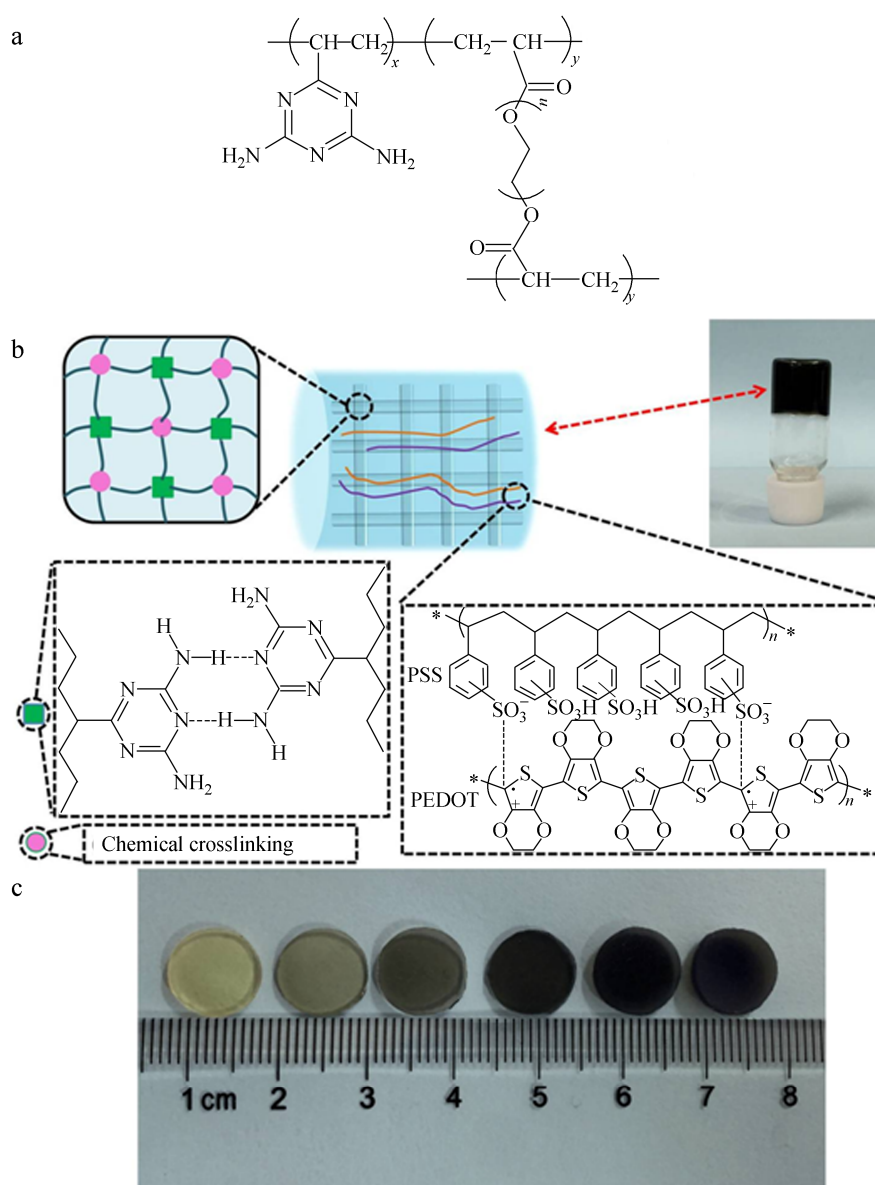


Fig. 1 (a) Schematic illustration of the molecular structure of poly(2-vinyl-4,6-diamino-1,3,5-triazine-*co*-polyethylene glycol diacrylates) (PVDT-PEGDA); (b) Schematic description of the network structure of PVDT-PEGDA-5 crosslinked by intermolecular hydrogen bonding and chemical crosslinking; (c) Photographs of PVDT-PEGDA-*X* hydrogels (from left to right in turn, *X* = 0, 1, 3, 5, 8, 10) (The online version is colorful.)

Fig. 1(b). Obviously, PVDT-PEGDA-5 hydrogels became dark blue after the addition of PEDOT/PSS, suggesting that the conductive component was firmly bound to the networks (Fig. 1b). Although the gels were immersed in water for a long time, no leaking of PEDOT/PSS was observed. And the colors of the conductive hydrogel have obviously changed with the addition of more PEDOT/PSS (Fig. 1c). Therefore, it is feasible to fabricate PVDT-PEGDA-*X* conductive hydrogels with different contents of conductive component incorporated in the matrices.

The fabrication of PEGDA is a key point for preparation of PVDT-PEGDA-*X* hydrogels. The $^1\text{H-NMR}$ spectrum (Fig. S1 in SI) indicates the formation of PEGDA by the following proton signals. $^1\text{H-NMR}$ (500 MHz, $\text{CDCl}_3\text{-d}_3$, δ): 6.39 (d, *cis* $\text{CH}_2=\text{CH}$), 5.83 (d, *trans* $\text{CH}_2=\text{CH}$), 6.16 (m, $\text{ROOCCH}=\text{CH}_2$), 4.28 (t, $\text{CH}_2=\text{CHCOOCH}_2-\text{CH}_2\text{O}-$), 3.58–3.64 (m, $-\text{CH}_2\text{CH}_2\text{O}-$)^[23].

Figures 2(A) and 2(B) display the ATR-FTIR spectra of the PVDT-PEGDA-0 and PVDT-PEGDA-5 hydrogels, respectively. It can be seen that the characteristic peaks at 3330 and 3200 cm^{-1} are assigned to the stretching vibrations of N–H in VDT, including symmetric and asymmetric stretches^[23]. Peaks at 1648 and 1540 cm^{-1} are ascribed to C=N and C–N stretching vibrations in VDT, respectively^[30, 31]. And the stretching vibration of $-\text{CH}-$ in the structure of PEGDA is located at 2870 cm^{-1} ^[23]. The characteristic peak at 1100 cm^{-1} is attributed to the stretching vibration of C–O–C in PEGDA^[23]. All those characteristic peaks demonstrate the successful copolymerization of VDT and PEGDA even with PEDOT/PSS.

The Raman spectra are shown in Fig. 2(C) (line b). The band at 990 cm^{-1} is assigned to oxyethylene ring deformation of PEDOT/PSS, and the broad absorption bands at 1365 and 1514 cm^{-1} are related to the asymmetric stretching deformation of $\text{C}\alpha-\text{C}\alpha$ and $\text{C}\beta-\text{C}\beta$, respectively^[17, 32, 33]. The peak at 1440 cm^{-1} is

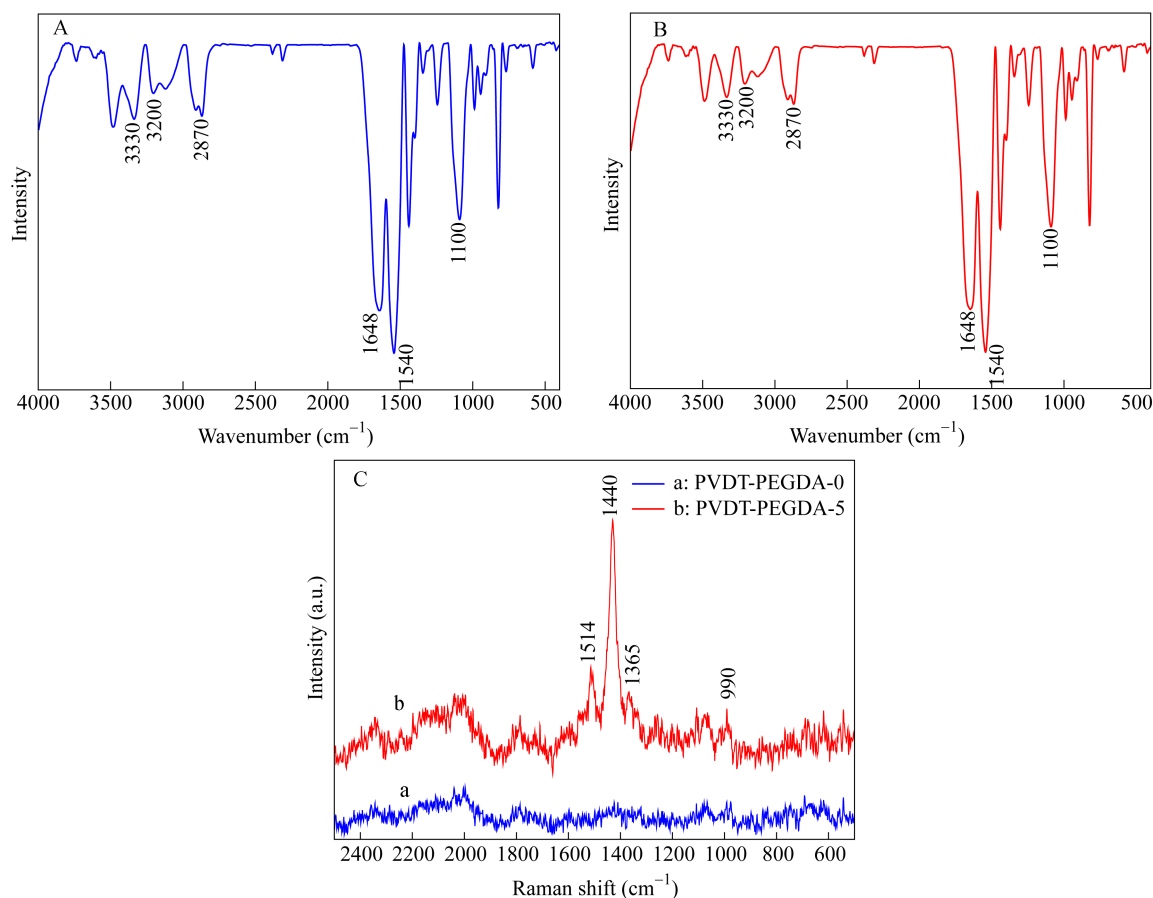


Fig. 2 ATR-FTIR spectra of (A) PVDT-PEGDA-0 hydrogel and (B) PVDT-PEGDA-5 hydrogel; (C) Raman spectra of PVDT-PEGDA-0 hydrogel (line a) and PVDT-PEGDA-5 hydrogel (line b)

ascribed to the symmetric stretching mode of the aromatic $C_{\alpha}=C_{\beta}$ in PEDOT^[17, 32, 33]. On the contrary, the intensities of those bands (Fig. 2C, line a) representing PVDT-PEGDA-0 hydrogels are rather weaker as compared with PVDT-PEGDA-5 containing PEDOT/PSS (Fig. 2C, line b). All the mentioned results indicate that PEDOT/PSS has been added into the hydrogel matrices.

Mechanical Properties

The above results revealed that PVDT-PEGDA-*X* are able to form stable conductive hydrogels owing to the combination of hydrogen bonding and chemical crosslinking. As a consequence, it is essential to study the mechanical strengths of PVDT-PEGDA-*X* hydrogels. It is worth mentioning that the obtained hydrogels are soaked into the deionized water to reach swelling equilibrium prior to the mechanical test. As shown in Fig. 3, the equilibrium water contents (EWCs) are measured to be in the range of 77.8%–83.8%. The inspection of EWCs reveals that the addition of PEDOT/PSS can improve the water content of hydrogels, which may be relevant with the hydrophilic performance of PSS. Furthermore, the as-prepared hydrogels were very stable in deionized water for a long time. Figures 4(a) and 4(b) demonstrate that the mechanical performances of PVDT-PEGDA-*X* gels are influenced by PEDOT/PSS to a different extent. Compared to the change in the tensile strength and Young's modulus of the PVDT-PEGDA-*X* hydrogels, adding PEDOT/PSS did not cause obvious variations of elongation at break, compressive strength and compressive modulus (Figs. 4a and 4b). Overall, the mechanical properties slightly deteriorated with the increase of PEDOT/PSS content (Table S2 in SI). An explanation is that the increase of PEDOT/PSS content leads to a slight reduction of hydrogen-bonded crosslinking density. In a word, while blending PEDOT/PSS in the system may only result in a slight disruption of hydrogen bonds, the EWC of PVDT-PEGDA-*X* hydrogels is increased with the increment of PEDOT/PSS content. On the other hand, we found that the hydrogels exhibited 0.48–1.20 MPa tensile strength, 7.58–9.52 MPa compressive strength, 1.55–2.59 MPa compressive modulus, 234.3%–274.6% breaking strain and 0.74–3.62 MPa Young's modulus, which clearly reflected the excellent mechanical properties of PVDT-PEGDA-*X* hydrogels. In addition, Figs. 4(c), 4(d), 4(e) and 4(f) show that the conductive hydrogels demonstrate an excellent ability to withstand large extension, compression, knotting and twisting. Our conductive hydrogels are far more mechanically stronger than the reported supramolecular conductive hydrogels and the chemically crosslinked conductive hydrogels^[34, 35].

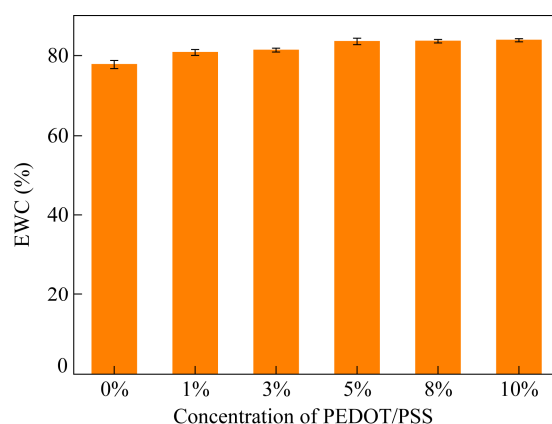


Fig. 3 The equilibrium water contents (EWCs) of PVDT-PEGDA-*X* hydrogels with different concentrations of PEDOT/PSS

Conductive Property

Figure 5 represents the conductivities of PVDT-PEGDA-*X* hydrogels. The change in hydrogel conductivity along with the variation of concentration of PEDOT/PSS exhibits the tendency of decrease first and then increase. In other words, when adding a small amount of PEDOT/PSS, the conductivity cannot be improved but reduced. When the contents of PEDOT/PSS are between 1% and 5%, the conductivities show a certain

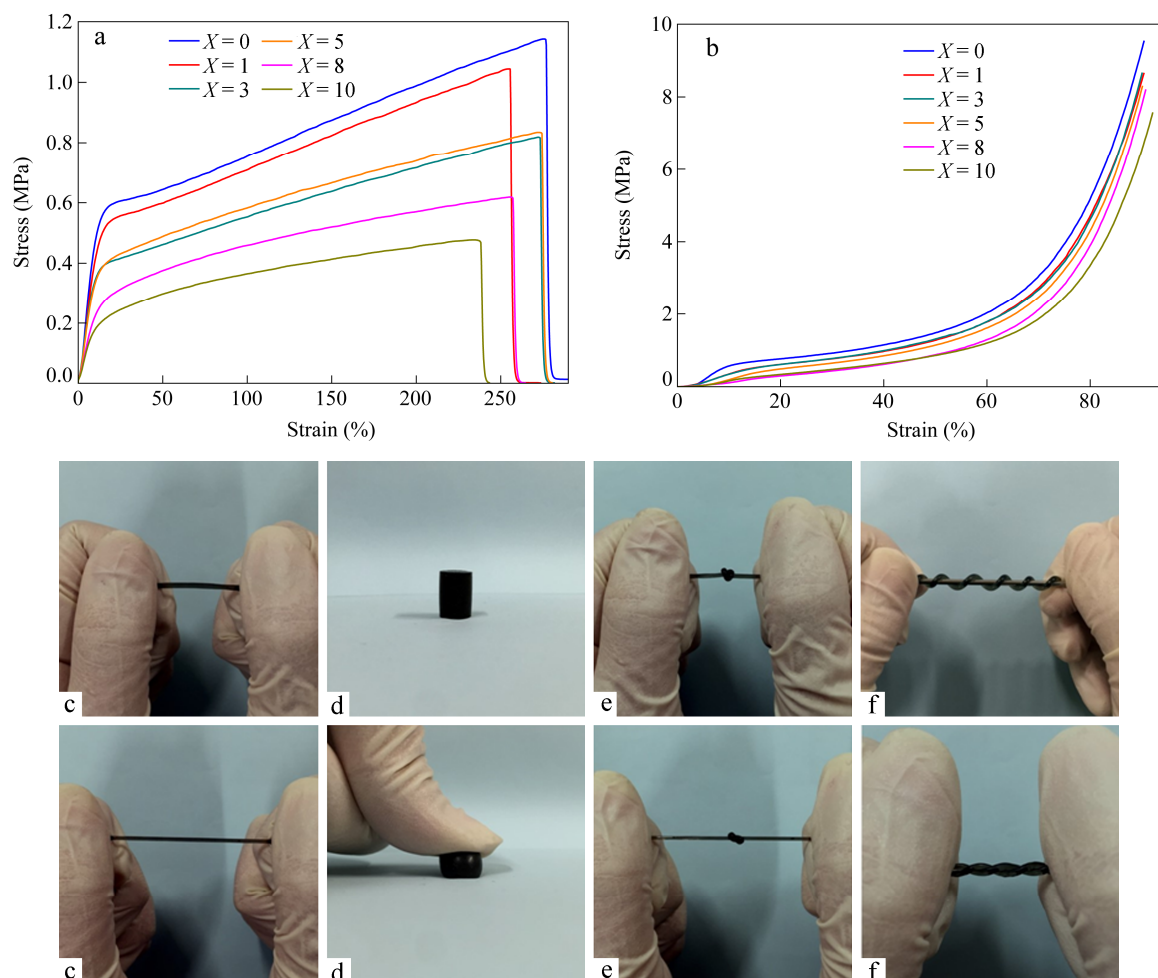


Fig. 4 (a) Tensile stress-strain curves and (b) compressive stress-strain curves of PVDT-PEGDA- X ; Photographs of PVDT-PEGDA-5 showing the ability to withstand (c) stretching, (d) compression, (e) knotting and (f) twisting (The online version is colorful.)

fluctuation but lower than PVDT-PEGDA-0. The reason for the undulation might be that a small amount of randomly dispersed conductive component caused the system a nonuniform structure, and thus could not form continuous transporting path for charge carriers to improve conductivity^[12, 34]. In contrast, with further increasing the content of PEDOT/PSS, there is a remarkable improvement of conductivities for the PVDT-PEGDA- X hydrogels, which is attributed to the more continuous transfer of charge carriers by plenty of PEDOT/PSS^[17, 34]. Therefore, it is evident that the presence of PEDOT/PSS in the hydrogels greatly enhanced the conductivities of the PVDT-PEGDA- X hydrogels, especially for the system with more amount of PEDOT/PSS. For example, the conductivity value of PVDT-PEGDA-10 hydrogel is up to $0.64 \text{ mS}\cdot\text{cm}^{-1}$, which is adequate to transfer bioelectrical signals *in vivo* and electrical stimulation on the cell proliferation and differentiation on account of the quite low microcurrent intensity in the human body^[34].

Cytotoxicity Assay *in Vitro*

MTT assay was used to evaluate the *vitro* cytotoxicity of the hydrogels. Figure 6 clearly shows that the cell viability is in the range of 76%–85%. More importantly, PEDOT/PSS has no adverse effect on the cell viability but can improve it a lot, which results from the biocompatibility of PEDOT/PSS. In other words, the conductive gels have better cytocompatibility. As a result, they exhibit great potential to be employed as a conductive biomaterial.

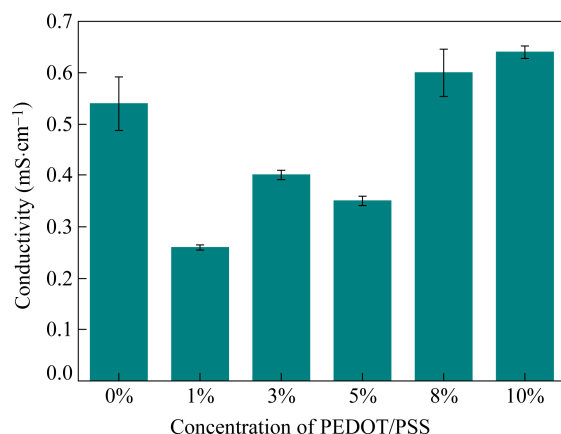


Fig. 5 Conductivities of PVDT-PEGDA-*X* hydrogels with different contents of PEDOT/PSS

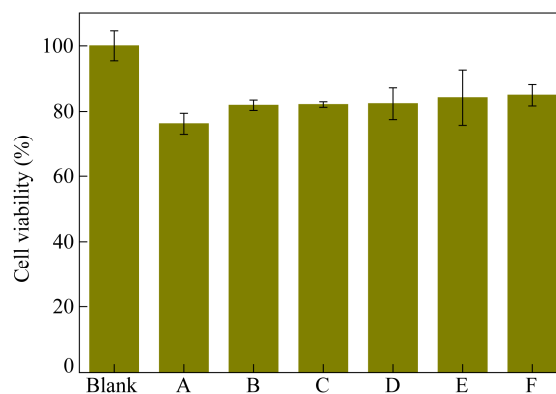


Fig. 6 Cytotoxicity results (represented by percentage cell viability) of different conductive hydrogel samples: (A) PVDT-PEGDA-0 hydrogel; (B) PVDT-PEGDA-1 hydrogel; (C) PVDT-PEGDA-3 hydrogel; (D) PVDT-PEGDA-5 hydrogel; (E) PVDT-PEGDA-8 hydrogel; (F) PVDT-PEGDA-10 hydrogel. Blank is the cells seeded on culture plate.

CONCLUSIONS

In summary, we have developed a convenient and versatile approach to fabricate high strength conductive hydrogels by simply *in situ* mixing the PVDT-PEGDA copolymer hydrogels to crosslink with multiple hydrogen bonds and the chemical cross linkages with PEDOT/PSS during the polymerization. The conductive hydrogels exhibited high mechanical tensile/compressive strengths with an excellent ability to withstand various deformations. Furthermore, PVDT-PEGDA-*X* hydrogels also possessed higher equilibrium water contents and higher conductivity up to 0.64 mS cm⁻¹ due to the addition of PEDOT/PSS. Importantly, the PVDT-PEGDA-*X* hydrogels showed better cytocompatibility. Hence, the PVDT-PEGDA-*X* hydrogels can be promising as biosensors, flexible electrode materials, and scaffold materials for soft tissue engineering.

REFERENCES

- Hur, J., Im, K., Kim, S.W., Kim, J., Chung, D.Y., Kim, T.H., Jo, K.H., Hahn, J.H., Bao, Z., Hwang, S. and Park, N., ACS Nano, 2014, 8(10): 10066
- Green, R.A., Baek, S., Poole-Warren, L.A. and Martens, P.J., Sci. Technol. Adv. Mater., 2010, 11(1): 014107
- Guisseppi-Elie, A., Biomaterials, 2010, 31(10): 2701
- Cheong, G.L.M., Lim, K.S., Jakubowicz, A., Martens, P.J., Poole-Warren, L.A. and Green, R.A., Acta Biomaterialia, 2014, 10(3): 1216
- Hao, G.P., Hippauf, F., Oschatz, M., Wissner, F.M., Leifert, A., Nickel, W., Mohamed-Noriega, N., Zheng, Z. and Kaskel, S., ACS Nano, 2014, 8(7): 7138
- Kumar, G.G., Hashmi, S., Karthikeyan, C., Nejad, A.G., Varnoosfaderani, M.V. and Stadler, F.J., Macromol. Rapid Commun., 2014, 35(21): 1861
- Wu, H., Yu, G., Pan, L., Liu, N., McDowell, M.T., Bao, Z. and Cui, Y., Nat. Commun., 2013, 4(3): 1943
- Li, L., Wang, Y., Pan, L., Shi, Y., Cheng, W., Shi, Y. and Yu, G., Nano Lett., 2015, 15(2): 1146
- Wang, E., Desai, M.S. and Lee, S.W., Nano Lett., 2013, 13(6): 2826
- Ahadian, S., Ramónazcón, J., Estili, M., Liang, X., Ostrovidov, S., Shiku, H., Ramalingam, M., Nakajima, K., Sakka, Y., Bae, H., Matsue, T. and Khademhosseini, A., Scientific Reports, 2014, 4(3): 4271

- 11 Dai, T., Qing, X., Lu, Y. and Xia, Y., *Polymer*, 2009, 50(22): 5236
- 12 Shi, Y., Ma, C., Peng, L. and Yu, G., *Adv. Funct. Mater.*, 2015, 25(8): 1219
- 13 Xia, Y. and Zhu, H., *Soft Matter*, 2011, 7(19): 9388
- 14 Ramónazcón, J., Ahadian, S., Estili, M., Liang, X., Ostrovidov, S., Kaji, H., Shiku, H., Ramalingam, M., Nakajima, K., Sakka, Y., Khademhosseini, A. and Matsue, T., *Adv. Mater.*, 2013, 25(29): 4028
- 15 Zhang, L. and Shi, G., *J. Phys. Chem. C*, 2011, 115(34): 17206
- 16 Bai, H., Sheng, K., Zhang, P., Li, C. and Shi, G., *J. Mater. Chem.*, 2011, 21(46): 18653
- 17 Kishi, R., Kubota, K., Miura, T., Yamaguchi, T., Okuzaki, H. and Osada, Y., *J. Mater. Chem. C*, 2014, 2(4): 736
- 18 Kishi, R., Hiroki, K., Tominaga, T., Sano, K.I., Okuzaki, H., Martinez, J.G., Otero, T.F. and Osada, Y., *J. Polym. Sci., Part B: Polym. Phys.*, 2012, 50(11): 790
- 19 Ding, H., Zhong, M., Kim, Y.J., Pholpabu, P., Balasubramanian, A., Hui, C.M., He, H., Yang, H., Matyjaszewski, K. and Bettinger, C.J., *ACS Nano*, 2014, 8(5): 4348
- 20 Dispenza, C., Lo Presti, C., Belfiore, C., Spadaro, G. and Piazza, S., *Polymer*, 2006, 47(4): 961
- 21 Phuchaduek, W., Jamnongkan, T., Rattanasak, U., Boonsang, S. and Kaewpirom, S., *J. Appl. Polym. Sci.*, 2015, 132(28): 42234
- 22 Zhang, Y., Li, Y. and Liu, W., *Adv. Funct. Mater.*, 2015, 25(3): 471
- 23 Zhang, J., Wang, N., Liu, W., Zhao, X. and Lu, W., *Soft Matter*, 2013, 9(27): 6331
- 24 Tang, L., Liu, W. and Liu, G., *Adv. Mater.*, 2010, 22(24): 2652
- 25 Bai, T., Zhang, P., Han, Y., Liu, Y., Liu, W., Zhao, X. and Lu, W., *Soft Matter*, 2011, 7(6): 2825
- 26 Crispin, X., Marciniak, S., Osikowicz, W., Zotti, G., Denier van der Gon, A.W., Louwet, F., Fahlman, M., Groenendaal, L., de Schryver, F. and Salaneck, W.R., *J. Polym. Sci., Part B: Polym. Phys.*, 2003, 41(21): 2561
- 27 Lin, P., Yan, F., Yu, J., Chan, H.L.W. and Yang, M., *Adv. Mater.*, 2010, 22(33): 3655
- 28 Ghosh, S. and Inganäs, O., *Adv. Mater.*, 1999, 11(14): 1214
- 29 Huang, H., Zeng, X., Li, W., Wang, H., Wang, Q. and Yang, Y., *J. Mater. Chem. A*, 2014, 2(39): 16516
- 30 Ren, Z., Zhang, Y., Li, Y., Xu, B. and Liu, W., *J. Mater. Chem. B*, 2015, 3(30): 6347
- 31 Tang, L., Yang, Y., Bai, T. and Liu, W., *Biomaterials*, 2011, 32(7): 1943
- 32 Teng, C., Lu, X., Ren, G., Zhu, Y., Wan, M. and Jiang, L., *Adv. Mater. Interfaces*, 2014, 1(6): 1400099
- 33 Du, G., Gao, G., Hou, R., Cheng, Y., Chen, T. and Fu, J., *Chem. Mater.*, 2014, 26(11): 3522
- 34 Huang, H., Li, W., Wang, H., Zeng, X., Wang, Q. and Yang, Y., *ACS Appl. Mater. Interfaces*, 2014, 6(3): 1595
- 35 Siddhanta, S.K. and Gangopadhyay, R., *Polymer*, 2005, 46(9): 2993