

Effects of oxidant and dopants on the properties of cellulose/PPy conductive composite hydrogels

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ABSTRACT: Cellulose/Polypyrrole (PPy) composite hydrogels were prepared by *in situ* chemically oxidative polymerization of pyrrole in the cellulose matrix. Ferric chloride (FeCl₃) was used as an oxidant and four sulfonic compounds were used as dopants in order to investigate the effects on the properties of cellulose/PPy conductive composite hydrogels. The extent of polymerization of PPy was determined by the amount of the oxidant and the composite hydrogels with oxidant at 0.3 M–0.5 M exhibited the higher conductivities for the intrachain and interchain conductivities of conductive polymers; the fracture stress of the composite hydrogels could be up to 26.25 MPa with a strain of 86.8% when the oxidant was at 0.5 M. Doping is an efficient way to improve the conductivity of the composite hydrogels and four kinds of dopant were compared in this work. Long alkane chain and side group in dopants can increase the steric hindrance of PPy polymerization which resulted in the lower conductivity of the composite hydrogels compared to dopants with smaller steric hindrance. The conductivity of the composite hydrogel firstly increased and then decreased with the concentration of dopants from 0.1 M to 1.0 M in this work. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43759.

KEYWORDS: cellulose and other wood products; conducting polymers; gels; mechanical properties

Received 28 November 2015; accepted 5 April 2016

DOI: 10.1002/app.43759

INTRODUCTION

In recent years, conductive composite hydrogels have been shown to change their swelling behaviors in response to electric fields^{1,2} and this characteristic makes their applications very attractive in biomedical sensors³, scaffolds for tissue engineering⁴, drug delivery,⁵ and electrode.⁶ According to previous studies, most of conductive hydrogels act shrinkage behavior in the electric field and shrinkage rate depends on voltage. The biocompatibility of electroactive polymers is commonly improved by embedding them in natural macromolecules. The combination of conductive polymers in a biodegradable hydrogel matrix with the structure of semi-interpenetrating network is minimally invasive and promising for future potential application as biomaterials. Zhao *et al.*⁴ found the way to *in situ* forming antibacterial and electro active degradable hydrogels, the conductivity and swelling ratio of hydrogels were studied. Zhao *et al.*⁷ synthesized electrically conductive hemicellulose hydrogels by cross-linking O-acetyl-galactoglucomanan with epichlorohydrin in the presence of conductive aniline pentamer in water and at ambient temperature. Alejandro *et al.*⁸ prepared the polyaniline/iota-carrageenan biocomposite hydrogel with intermolecular interactions of ionic and hydrogen bonds. The conductive polythiophene/chitosan/carboxymethylchi-

tosan hydrogel were prepared by Datchanee *et al.*⁹ which showed the good response to an applied electric field with the potential application as implantable artificial muscles. Shin *et al.*¹⁰ investigated chitosan/polyaniline semi-interpenetrating network polymers under different pH conditions. Tai¹¹ and Qu¹² use the alginate as matrix to obtain the conductive hydrogels with various conductive substances. However, some of these biodegradable polymers are not feasible to fabricate the hydrogels and some of them form the physical hydrogels with low mechanical properties.

Cellulose, the most abundant renewable macromolecule on the earth, can also be applied to preparing composite hydrogels as matrix with fascinating structures and properties for its abundant hydroxyl groups.¹³ Nyström coated the individual fibers of wood-based nanocellulose in the hydrogel with polypyrrole to obtain an electrically conducting continuous high-surface-area composite.¹⁴ Shi *et al.*¹⁵ and Kim *et al.*¹⁶ combined bacterial cellulose hydrogels with polyaniline and carbon nanotube respectively to assembly the conductive composite hydrogels. In our previous work,¹⁷ cellulose-based conductive hydrogels was developed by compositing microcrystalline cellulose (MCC) hydrogel with polypyrrole to form the semi-interpenetrating network. MCC was firstly dissolved in ionic liquid and chemically crosslinked to prepare the hydrogel and PPy were formed

Table I. Conductivity of Cellulose/PPy Composite Hydrogels at Various Concentration of FeCl₃

Sample ^a	1	2	3	4	5
Concentration of FeCl ₃ /(M)	0.1	0.3	0.5	0.7	0.9
Electrical Conductivity/(S cm ⁻¹)	6.20 × 10 ⁻³	9.18 × 10 ⁻³	7.83 × 10 ⁻³	5.88 × 10 ⁻³	2.35 × 10 ⁻³

by *in situ* chemically oxidative polymerization of pyrrole in the matrix. This is a simple and convenient approach to prepare cellulose-based conductive hydrogels with high conductive and good mechanical properties.

The conductive and mechanical properties of the composite hydrogels are mainly determined by the structure and distribution of conductive components. Polymers such as PPy and polyaniline are electronically conductive due to the presence of conjugated double bonds and their conductivity is acquired by doping with electron-donor or electron-acceptor agents. Small molecular dopants have been widely applied to improve the conductivity of conductive polymers though some polymeric dopants were reported to be used to decrease the de-doping reactions of the small dopants.^{18,19} PPy has attracted considerable interest due to easy synthesis by *in situ* chemical polymerization and long-term stability of conductivity. When the pyrrole is oxidatively polymerized into long chain polymer, the obtained polymer possesses positive charge which is electroneutralized by the incorporation of dopant anions. The morphology, conductivity and mechanical strength of PPy conductive composites are greatly dependent on the oxidant and the dopant. Many reports are concentrated on the effects of the oxidant and doping on the conductive composites such as film^{20,21} and fiber^{18,22–24}; however, there is limited knowledge on the hydrogels.

In this article, effects of the oxidant and dopants on the properties of as-prepared cellulose/PPy conductive composite hydrogels were systematically investigated. Both conductivity and mechanical properties were controlled by the oxidant and dopants. The morphology, elements composition, and thermal stability of the conductive composite hydrogels were also characterized.

EXPERIMENTAL

Materials

Microcrystalline Cellulose (MCC) was purchased from National Medicine Group Chem (China) and used as received. 1-butyl-3-methylimidazolium chloride (BMIMCl), benzoyl peroxide (BPO), dimethylacetamide (DMAc), ferric chloride (FeCl₃), HCl, sodium benzene sulfonate (BSNa), sodium dodecylbenzene sulfonate (DBSNa), 2-naphthalene sulfonic acid (NSA), and sodium p-toluenesulfonate (TsONa) were of analytical grade and used without further purification. N,N-methylene bisacrylamide (BIS) was of analytical grade and recrystallized from ethanol before using. Pyrrole (Py) monomer was distilled under reduced pressure and stored at 3 °C in a dark area.

Preparation of the Conductive Composite Hydrogels

Cellulose/PPy conductive composite hydrogels were prepared according to the procedure in the previous work¹⁷ and various dopants were applied in the preparation. The electrical conductivities were measured via the four-probe method at room

temperature by inserting four probes into cylinder hydrogel samples with the diameter of 21 mm and thickness of 3mm (KDY-1 4-Point probes resistivity measurement system, Kunde Science, China).

Characterizations

Mechanical Properties. The compressive stress–strain measurements (INSTRON5565, Instron Co., USA) were performed to reveal the mechanical properties. The composite hydrogel with the dimension of 10 mm × 8 mm × 5 mm was set on the lower plate and compressed by the upper plate, which was connected to a load cell, at a strain rate of 2% min⁻¹.

Morphology. The composite hydrogels were quenched with liquid nitrogen and freeze-dried after crosscut. The samples were mounted on metal disk and coated with gold; the microstructures were observed and photographed via a scanning electron microscope (S3700N, Hitachi, Japan).

Elemental Analysis. The chemical element composition of the composite hydrogels was determined by elemental analysis using an elemental analyzer (EA, Vario EL cube, Elementar, Germany).

Thermal Stability. Thermogravimetric analysis (TGA) of the composite hydrogels were performed on a thermal analyzer (STA449E, NETZSCH, German) using ~5–10 mg of the sample under nitrogen at a heating rate of 10 °C min⁻¹ from the ambient temperature to 700 °C.

RESULTS AND DISCUSSION

Effects of Oxidant

Effects on the Conductivity. The electrical conductivities of the composite hydrogels are mainly determined by the oxidant and dopants in this work. The conductive component of PPy was obtained by oxidative polymerization by Py monomer with FeCl₃, therefore the extent of polymerization and conductivity were influenced by the amount of the oxidant. Electrical conductivities of cellulose/PPy composite hydrogels at various concentrations of FeCl₃ are shown in Table I. With the increasing of the FeCl₃ concentration, the electrical conductivity of the composite hydrogels increased firstly and then decreased. The composite hydrogels obtained the higher electrical conductivity when the concentration is ranged from 0.3 M to 0.5 M. The conductivity of conductive polymers is the combination of the intrachain and interchain conductivities. The intrachain conductivity is mainly determined by the regularity and molecular weight of the polymer. The conjugation length of PPy was decreased to some extent by over oxidation of pyrrole with the excess oxidant which jeopardized the intrachain conductivity.^{25,26} Meanwhile, the interchain conductivity is affected by the transportation of charge carriers from one chain to others²⁷ and well-packed structure between polymer chains is benefit to increase the conductivity. At high concentration of FeCl₃,

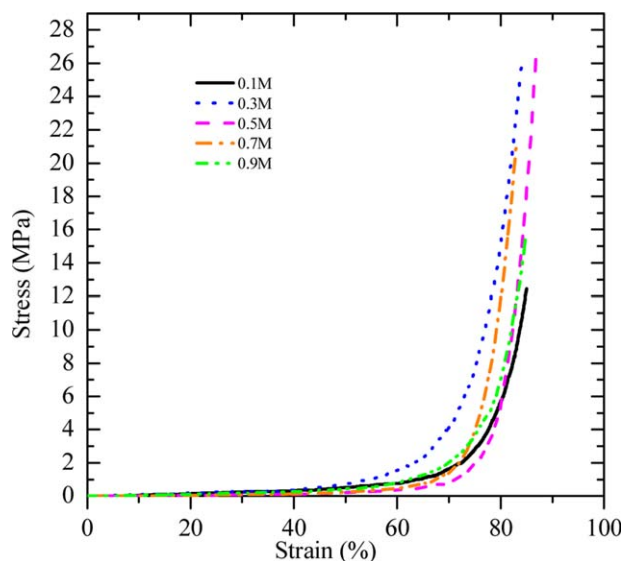


Figure 1. Compressive stress-strain curves of MCC/PPy composite hydrogel doped with TsONa at various FeCl_3 concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peroxidation of PPy is easy to be caused and C—OH will be generated at β -C of Py which can be converted to C=O easily. Therefore, the electrical conductivities of PPy is reduced because of the destroyed conjugate structure of PPy.^{23,28} Therefore, the composite hydrogels with oxidant at appropriate concentrations exhibited the higher conductivities for the better packed structure of the hydrogel networks.

Effects on the Mechanical Property. For conductive composite hydrogels, the lack of mechanical property is probably the most obvious and intractable problem, which greatly obstructs their applications in the field of biomedical materials such as biological electrical sensor, artificial scaffold, and articular cartilage.²⁹ Therefore, both conductive and mechanical properties are important to the conductive composite hydrogels. Figure 1 shows the stress-strain curves of the composite hydrogels doped with TsONa at various FeCl_3 concentrations. It can be seen that with the increasing of the concentration, the mechanical strength of the composite hydrogels showed the trend of increasing firstly and then decreasing. When the concentration of the oxidant was 0.1 M, the composite hydrogel could sustain a strain of 85.0% with fracture stress of 12.42 MPa; while the fracture stress of the composite hydrogels obtained with both 0.3 M and 0.5 M FeCl_3 could be up to 26.25 MPa, meanwhile the composite hydrogel at 0.5 M of FeCl_3 could sustain a strain of 86.8% whereas the one at 0.3 M was 83.8%. However, both the fracture stress and strain of the composite hydrogels were reduced with the concentration of FeCl_3 further increasing. The fracture stress of the composite hydrogels with 0.7 M and 0.9 M were further decreased to 21.00 MPa and 15.51 MPa along with the fracture strain of 83.0% and 85.0%, respectively. In the composite hydrogels, the polymer chains of PPy were scattered in the MCC hydrogel to form the semi-interpenetrating network and the chain length was a key parameter to the mechanical property of the composite hydrogel. The length of PPy could be decreased by over oxidation at high concentrations of FeCl_3 and short chains of PPy acted as defects

resulting in the lowered mechanical property. As an external stress is applied, the local stress cannot be effectively transferred from the MCC matrix to PPy component which jeopardize the energy dissipation and mechanical strength. Therefore, the proper concentration of FeCl_3 was set at 0.5 M with the combination of the effects of oxidant on the both conductivity and mechanical strength of the composite hydrogels. *The concentrations of Py and TsONa in the preparation of the composite hydrogels were 0.15 M and 0.75 M, respectively.

Morphology Analysis. The cross-section of the composite hydrogels was characterized to further identify the morphology of the hydrogels with various oxidant concentrations. As shown in Figure 2, it is obvious that the PPy granules [Figure 2(a)] or clusters [Figure 2(d,e)] were found to attach to the hydrogel network which might result in the poor conductive and mechanical performances at these concentrations of the oxidant. However, homogeneous MCC network with the uniformly distributed PPy components was formed when the concentrations of FeCl_3 were 0.3 M and 0.5 M [Figure 2(b,c)], moreover the honeycomb-like structure without visible PPy granules or clusters would not be ready to cause the stress concentration and undesirable interchain conductivity.

Effects of Dopants

Effects of Types on the Conductivity. Doping is an efficient way to improve the conductivity of the composite hydrogels. Table II presents the results of the elemental analysis and conductivities of PPy/cellulose composite hydrogels obtained with various dopants. The conductivity of the doped composite hydrogels reaches the order of magnitude of 10^{-2} which is applicable for biomaterials except for those with DBSNa and TsONa. Especially, the composite hydrogel doped with BSNa showed the most enhanced conductivity up to $1.1 \times 10^{-2} \text{ S cm}^{-1}$. It is known that the conductivity of conducting polymers mainly depend on the regularity of polymer (conjugation length) and inter-chain packing.³⁰ Moreover, the *S/N* ratio represents the doping level for one pyrrole ring in the PPy chain³¹ which is related to the conductivity of the composite hydrogel to some extent. For the composite hydrogel, higher *S/N* ratio is corresponding to the higher conductivity except for the one with TsONa. Although the nucleophilicity and electronegativity of doped particles are critical factors of the conductivity of PPy, it is also affected by the composition and volume of dopant molecules. In this case, the large molecular volume of TsONa can be a steric barrier for the pyrrole radical cations oligomerization and later for the creation of PPy chains.³¹

Effects of Concentration on the Conductivity. In order to further reveal the function of dopants, the effects of concentration on the conductivity of the composite hydrogels are shown in Figure 3. Generally, the conductivity of the composite hydrogel firstly increased and then decreased with the concentration of dopants from 0.1 M to 1.0 M. In the energy band structure of PPy, Fermi level is located between conduction band and valence band, the energy difference between conduction band and valence band was decreased by reducing the mobile resistance of charge carriers when PPy was doped. Meanwhile, the regularity of PPy chain was enhanced after the initial doping

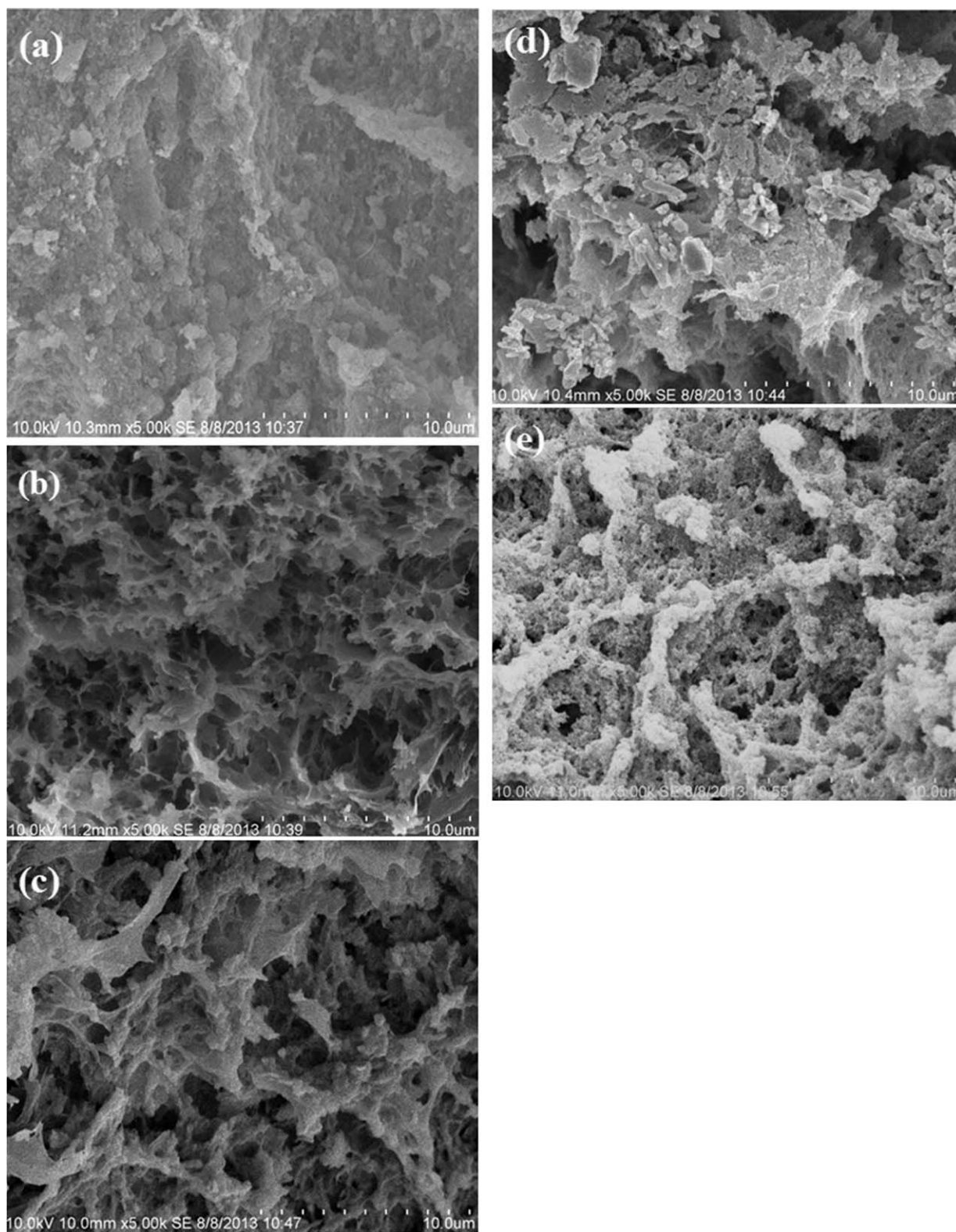


Figure 2. SEM images of the cross-section of PPy/cellulose composite hydrogels. FeCl_3 concentration: (a) 0.1M; (b) 0.3M; (c) 0.5M; (d) 0.7M; (e) 0.9M.

process. Both the narrowed energy gap and improved chain regularity are benefit to enhance the conductivity of the composite hydrogels to some extent. However, the excess of the acid doped obstructs the molecular chain of PPy to form the perfect con-

ductive structure; therefore PPy with insulation defect considerable influences the charge-carrier transport and finally the conductivity of the composite hydrogels. Moreover, the configuration of the dopants can influence the conductivity of the PPy,

Table II. Elements Composition and Conductivity of PPy/Cellulose Composite Hydrogels with Various Dopants

Dopant ^a	C1s (at %)	N1s (at %)	O1s (at %)	S2p (at %)	S/N	Conductivity ^b (S cm ⁻¹)
BSNa	44.85	12.98	34.60	1.395	0.1075	1.1×10^{-2}
DBSNa	37.08	11.69	34.21	0.041	0.0035	1.43×10^{-3}
NSA	50.80	6.00	33.67	0.591	0.0985	1.01×10^{-2}
TsONa	43.07	10.04	32.46	2.637	0.2626	7.83×10^{-3}

long alkane chain of DBSNa can be a spacer to PPy polymerization and side group in TsONa also increased the steric hindrance of the reactions compared to BSNa which resulted in the low conductivity of the composite hydrogels doped with DBSNa and TsONa.

Effects of Types on the Thermal Stability. Thermal stability of the composite hydrogels doped with various dopants is presented in Figure 4. In the first temperature range from 25 °C to 140 °C, the absorbed water and bound water were removed from the composite hydrogels and the weight loss was about 17%. The composite hydrogels with various dopants almost kept constant weight from 140 °C to 240 °C which indicated the excellent thermal stability, and then the main mass loss corresponding to PPy degradation and cellulose thermal decomposition started at about 260 °C and 340 °C.

CONCLUSIONS

In this work, effects of the oxidant and dopants on the properties of obtained cellulose/PPy conductive composite hydrogels were investigated. The conductivity, mechanical property, and morphology are mainly determined by the concentration of the oxidant for the various extent of polymerization. With the increasing of the FeCl₃ concentration, both the electrical conduc-

tivity and mechanical strength of the composite hydrogels increase firstly and then decrease. When the concentrations of FeCl₃ are 0.3 M and 0.5 M in this work, the composite hydrogels show the excellent conductive and mechanical properties up to 9.18×10^{-3} S cm⁻¹ and 26.25 MPa. Moreover, doping is an efficient way to improve the conductivity of the composite hydrogels. The conductivity of some doped composite hydrogels reaches the order of magnitude of 10⁻² which is applicable for biomaterials. Compared to BSNa and NSA, long alkane chain of DBSNa and side group in TsONa can increase the steric hindrance of PPy polymerization resulting in the lower conductivity of the doped composite hydrogels. Based on the results of this work, the conductivity and mechanical properties of the cellulose/PPy composite hydrogels are controllable by adjusting the oxidant and dopants. In the future work, the potential application of cellulose/PPy composite hydrogel in drug delivery and artificial muscle will be investigated.

ACKNOWLEDGMENTS

This work was supported by the National Nature Science Foundation of China (Grant No. 31200457) and NSERC Innovative Green Wood Fibre Network (Canada).

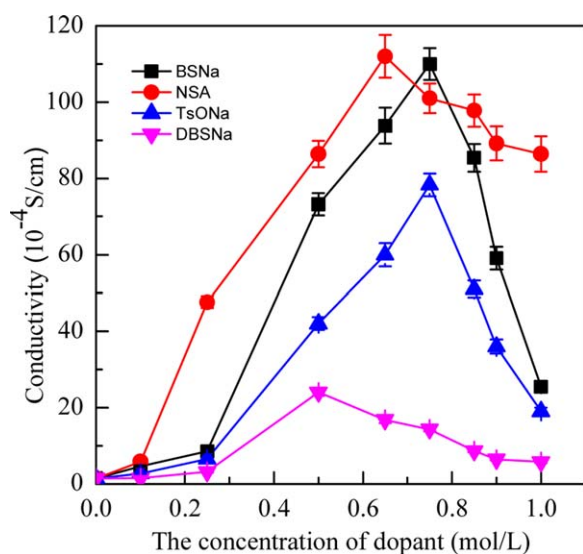


Figure 3. The relationship of conductivity of PPy/cellulose composite hydrogel with the concentration of dopants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

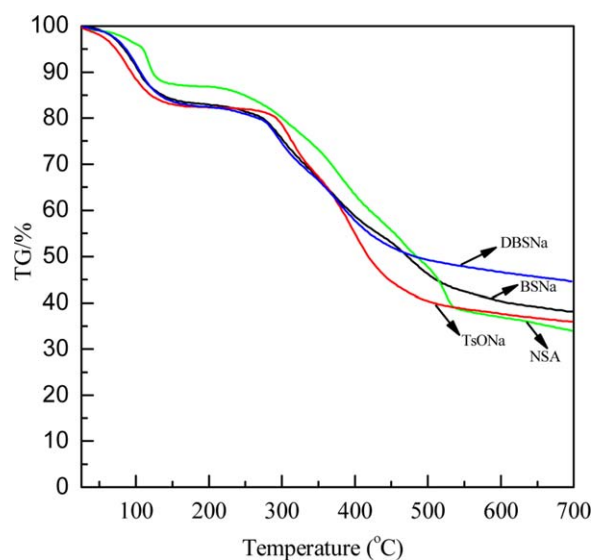


Figure 4. TGA curves of MCC/PPy composite hydrogels doped with various dopants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

REFERENCES

1. Karbarz, M.; Gniadek, M.; Donten, M.; Stojek, Z. *Electrochem. Commun.* **2011**, *13*, 714.
2. Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242.
3. Li, L.; Wang, Y.; Pan, L.; Shi, Y.; Cheng, W.; Shi, Y.; Yu, G. *Nano Lett.* **2015**, *15*, 1146.
4. Zhao, X.; Li, P.; Guo, B. L.; Ma, P. X. *Acta Biomater.* **2015**, *26*, 236.
5. Ge, J.; Neofytou, E.; Cahill, T. J.; Beygui, R. E.; Zare, R. N. *ACS Nano.* **2012**, *6*, 227.
6. Mario Cheong, G. L.; Lim, K. S.; Jakubowicz, A.; Poole-Warren, L. A.; Green, R. A. *Acta Biomater.* **2014**, *10*, 1216.
7. Zhao, W. F.; Glavas, L.; Odelius, K.; Edlund, U.; Albertsson, A. C. *Chem. Mater.* **2014**, *26*, 4265.
8. Alejandro, V. R.; Jorge, L. O. M.; Bárbara, F. M.; Claudia, A. H. E. E.; Armando, Z. C. *Carbohydr. Polym.* **2014**, *110*, 78.
9. Datchanee, P.; Pornpun, Y.; Sutawan, J.; Siripong, T.; Pikulthong, C. *Energy Procedia* **2013**, *34*, 673.
10. Shin, S. R.; Park, S. J.; Yoon, S. G.; Spinks, G. M.; Kim, S. I.; Kim, S. J. *Synth. Met* **2005**, *154*, 213.
11. Tai, Y. L.; Mulle, M.; Ventura, I. A.; Lubineau, G. *Nanoscale* **2015**, *7*, 14766.
12. Qu, B.; Chen, C. S.; Qian, L. Y.; Xiao, H. N.; He, B. H. *Mater. Lett.* **2014**, *137*, 106.
13. Prabakaran, M.; Mano, J. F. *Macromol. Biosci.* **2006**, *6*, 991.
14. Nyström, G.; Mihranyan, A.; Razaq, A.; Lindström, T.; Nyholm, L.; Strømme, M. *J. Phys. Chem. B* **2010**, *114*, 4178.
15. Shi, Z. J.; Zang, S. S.; Jiang, F.; Huang, L.; Lu, D.; Ma, Y. G.; Yang, G. *RSC Adv.* **2012**, *2*, 1040.
16. Kim, Y. H.; Park, S.; Won, K.; Kim, H. J.; Lee, S. H. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 1067.
17. Liang, X. T.; Qu, B.; Li, J. R.; Xiao, H. N.; He, B. H.; Qian, L. Y. *React. Funct. Polym.* **2015**, *86*, 1.
18. Wang, H. H.; Hu, M. M.; Fei, G. Q.; Wang, L.; Fan, J. *Cellulose* **2015**, *22*, 3305.
19. Fonner, J. M.; Forciniti, L.; Nguyen, H.; Byrne, J.; Kou, Y. F.; Syeda-Nawaz, J.; Schmidt, C. E. *Biomed. Mater.* **2008**, *3*, 034124.
20. Balkan, T.; Sarac, A. S. *Fibers Polym.* **2011**, *12*, 565.
21. Lim, T. H.; Oh, K. W.; Kim, S. H. *J. Appl. Polym. Sci.* **2012**, *123*, 388.
22. Wang, N.; Li, G. D.; Yu, Z.; Zhang, X. X.; Qi, X. L. *Carbohydr. Polym.* **2015**, *127*, 332.
23. Cetiner, S. *Text. Res. J.* **2014**, *84*, 1463.
24. Ding, C. Y.; Qian, X. R.; Yu, G.; An, X. H. *Cellulose* **2010**, *17*, 1067.
25. Ren, L.; Zhang, X. F.; Wang, L. X.; Zhang, F. Q. *Chinese J. Semiconductors* **2007**, *28*, 1396.
26. Lin, S. L.; Cao, X.; Lin, Q.; Chu, Y. W.; Guo, Y. D.; Long, D.; Wan, Y. *J. Jiangsu Univ. Sci. Technol. (Natural Science Edition)* **2010**, *24*, 353.
27. Wan, M. X.; Li, J. C. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 2359.
28. Fu, C. J.; Li, S.; Zhao, W. L.; Zhang, J. *Heilongjiang Univ. Sci. Technol.* **2014**, *24*, 0612.
29. Dai, T. Y.; Qing, X. T.; Lu, Y.; Xia, Y. Y. *Polymer* **2009**, *50*, 5236.
30. Raudsepp, T.; Marandi, M.; Tamm, T.; Sammelselg, V.; Tamm, J. *Electrochim. Acta* **2008**, *53*, 3828.
31. Omastová, M.; Trchová, M.; Kovářová, J.; Stejskal, J. *Synth. Met.* **2003**, *138*, 447.