



Fabrication, characterization and application of chitosan/tea polyphenols blending hydrogels

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Abstract. Taking the chitosan (CS) to blend with the tea polyphenols (TP) a CS/TP hydrogel was fabricated. Results showed that this fully green hydrogel has a water content at about 54% and a tensile strength within 10–13 MPa capable for applying to the soft contact lens (SCL) By controlling the added TP percent at 1–2 wt%, this CS/TP hydrogel presented good anti-ultraviolet (UV) property fitting the standards of the class-1 of SCL of US Food and Drug Administration.

Keywords. Chitosan; tea polyphenols; hydrogel; soft contact lens; anti-ultraviolet.

1. Introduction

Soft contact lens (SCL) has been long time used by people in the fields of vision correction, therapeutics and cosmetics [1–14]. Recently reports showed that the SCL can also be applied as a biosensor for ophthalmic health monitoring by integrating the electronics, intraocular pressure or both [15–17].

In general, the SCL was produced by using some synthetic polymers, e.g., the polymethyl acrylates hydroxyethyl (PHEMA), *N*-vinylpyrrolidone (NVP) and polyvinyl alcohol (PVA) [3]. However, these synthetic polymers-based SCLs have been found to cause some problems for people [4,5,8,15–17]. Therefore, some special SCLs, e.g., the drug-based SCLs, were developed as reported elsewhere [12–14,18–21].

Ultraviolet radiation, UVR, from the sun is a typical aspect for the hard sunglasses and has been divided into different UV ranges, e.g., UV-C in the range of 100–290 nm [22] or 200–280 nm [23], UV-B in the range of 290–320 nm [22] or 280–315 nm [23] and UV-A in the range of 320–400 nm [22] or 315–400 nm [23] by World Health Organization (WHO) [22] and ICNIRP (International Commission on Non-Ionizing Radiation Protection) [23], respectively. It is known that all UV-C and about 90% UV-B can be absorbed by the ozone layer, and the UV-A and a small percentage of UV-B can reach the earth surface and affect people, especially the eyes [22,24]. Of these UVR, the UV-B is

associated with the corneal damage, the UV-A is far less photo-biologically active with deeper penetration than the UV-B, and the UV-A may pose more of a long-term hazard due to presence in solar radiation higher than that of the UV-B and UV-C [22,24].

On the eyes, the UVR exposure is strongly associated with the development of pterygium, photo keratitis, climatic droplet keratopathy and cortical cataracts [25,26]. It is also known that the initial anti-UV SCL was reported in 1987 [27] and then broadly developed by applying some UV-absorbing or -blocking materials to blend with the synthetic polymers [28–38].

Chitosan (CS) is a typical biopolymer broadly applied in biomedical area [39–41] and has been recently applied to coat the SCL surface to enhance the release of drugs [42,43]. Recently, Jeenchama *et al* [44] have used CS to produce a novel daily disposable therapeutic SCL for the ophthalmic delivery of diclofenac sodium, where these researchers blended the regenerated silk fibroin in CS-based SCL for enhancing the required strength.

The aim of this work is to apply the CS as a raw material to produce the anti-UV SCL. Experimentally, the tea polyphenols (TP) was employed to mix with the CS solution to cast the CS/TP blend-based SCL in a patterned die. In such design, the CS/TP composite was considered to keep the good antioxidant and antibacterial properties as literature reported elsewhere [45–47] while with good anti-UV properties in terms of TP provided possibility [48].

2. Experimental

2.1 Materials

A commercial powder CS supplied by Shanghai Tian-Qing Biomaterial Company was used as received. According to this company, this CS has a viscosity at about 625 mPa S and a degree of deacetylation at 91.2% [49–53].

The employed TP was purchased from Xuancheng Baicao Plants Industry and Trade Co., Ltd. China, and used as received [48,54–56]. According to the producer, this TP has the polyphenols at 99.3%, theine at 0.2% and ash less 0.3%.

2.2 Fabrication of CS/TP-based anti-UV SCL

A CS solution was initially prepared by dissolving the powder sample in acetic acid at 2 wt%, then TP with different weights were added and dissolved in this CS solution to form the CS/TP mixed solutions at a concentration of 1, 2, 3 and 5 wt%, respectively. After de-aeration and filtration, the CS/TP mixed solution was patterned in a ceramic die to form the SCL, then evaporated and dried at 45°C in an oven until the weight stabilized. The dried sample was immersed in a NaOH (2%) solution to neutralize the residual acid then washed by water for several times. Finally, the sample was cross-linked by immersing in the citric acid (8%) for solidification.

2.3 Characterization

The morphology was analysed by scanning electron microscope (SEM) JSM-5600LV, with an accelerating voltage of about 10 kV.

The water content was measured as in equation below. The oven-dried sample was initially swollen in water until up to the weight stabilized, then measured as the weight, W_1 (g). The wet sample was vacuum oven dried until the weight stabilized then measured as W_2 (g), all at 25.0 ± 0.1°C, humidity at 70% condition. The water content was estimated according to equation (1).

$$\text{SCL}_{\text{water}} (\%) = (W_1 - W_2) / W_1 \quad (1)$$

Tensile strength was measured using a WDW3020 test machine (Changchun Kexin Experiment Instrument Co, China). During measurement, the drawing rate was set at 10 mm min⁻¹, and each value was averaged by measuring five samples. The measurement temperature was at 25.0 ± 0.1°C.

The structure was analysed by a Nicolet NEXUS-670 FTIR spectrometer. The presented Fourier transform infrared (FTIR) spectra were recorded from 400 to 4000 cm⁻¹ by scanning 10 times in a resolution of 4 cm⁻¹.

The anti-UV property was measured by the Ultra-Violet Transmittance Fabric Analyzer (UV-1000F, Labsphere Co.

USA). The recorded spectra were in the range of 200–800 nm in relation to both the UV-ray transmission range and visible-light transmission range.

3. Results and discussions

3.1 Morphology, water content and tensile strength of CS/TP-based SCL

As the product is to be in direct eye contact, SCL needs certain surface smooth to fit this application [57]. Figure 1 presents and compares the SEM images of the pure CS-based common SCL (left) and CS/TP-based SCL with 5 wt% TP (right). Though the characterization of surface smooth on the basis of SEM seems to be rough, the comparison, however, can indicate that the common pure CS sample presented smooth surface with dense structure (figure 1, left) and the CS/TP sample presented also a smooth surface while with some white dots (figure 1, right). This is in good agreement with literature reported CS samples [44] and commercial SCL samples, e.g., Acuvue 2, Acuvue Advance, Focus Dailies, Precision etc. [57].

The surface smooth of SCL is mainly controlled by processing the used materials [57]. According to Guryca *et al* [57], the surface smooth of SCL is strongly influenced by water content. It is reasonable because the CS/TP formed hydrogel has strongly hydrogen bonding to benefit the surface smooth.

The water content of these TP-free and TP-based two SCLs has been found both at about 54% greater as compared with literature reported values [43,58] and commercial samples [57] as expected for SCL [57].

Mechanical properties are of importance for SCL application [7,58]. The required values for SCL issued by Chinese standard for hydrogen SCL are summarized in table 1. Since our samples have a water content at about 54% and the tensile strength within 10–13 MPa, these values indicated that the pure CS- and CS/TP-based SCLs both are qualified to fit the Chinese standard, and well agreed with literature reported cases [46].

3.2 Structure of CS/TP-based SCL

The FTIR spectra of the CS/TP-based SCLs with TP percent at 1, 3 and 5% are presented in figure 2 with the referenced pure CS and TP, respectively.

Observe the pure CS presented intense peaks at 3430 due to the O–H stretching and amine N–H symmetric vibrations, 2890 due to C–H stretching, 1597 due to the N–H bending and C–H vibration of amide II, 1389 due to the C–CH₃ vibration, 1157 and 1071 due to the C–O vibration of saccharide molecules, and 896 cm⁻¹ due to the C–C stretching vibrations of the polysaccharide molecules [15,44,46]. The pure TP showed intense peaks at 3430 due to the O–H

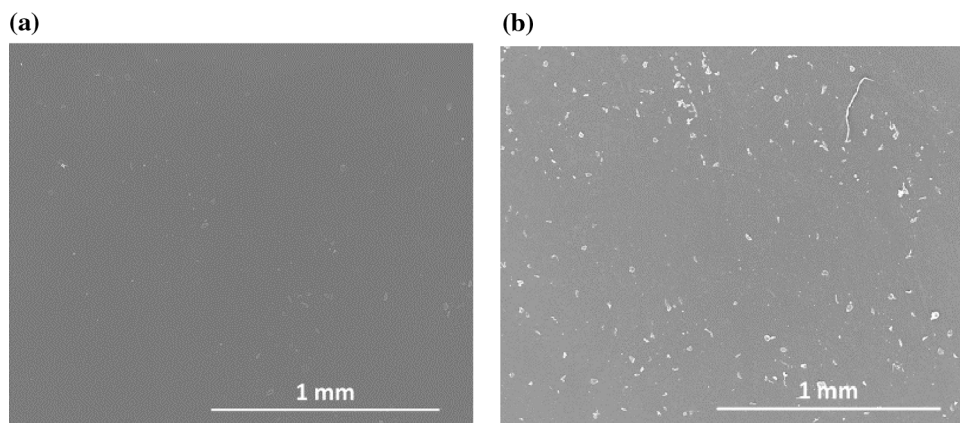


Figure 1. SEM images of pure CS-based SCL (a) and CS/TP-based SCL (b).

Table 1. Chinese standard (GB11417.2-89) on the mechanical properties of hydrogen SCL.

Hydrogen SCL	
Water (%)	Tensile strength (MPa)
≤ 49	8.0
> 49 to < 70	4.5
≥ 70	4.0

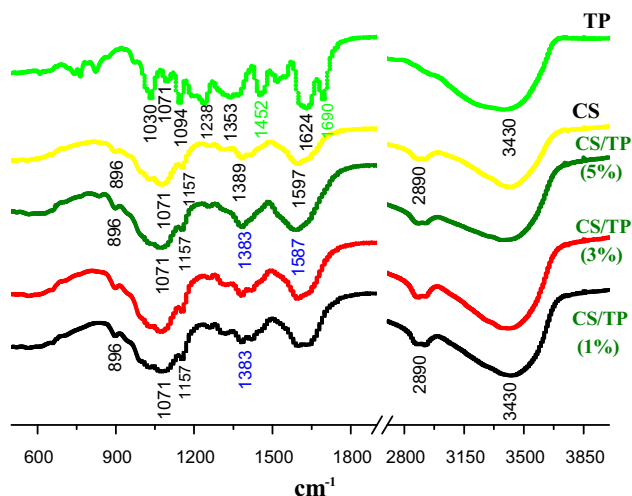


Figure 2. FTIR spectra of CS/TP-based SCL with TP percent at 1, 3 and 5 wt%, and referenced pure CS and TP, respectively.

stretching, 1690 due to the C=O stretching, 1624 due to the aromatic C=C stretching, 1452 due to the C–H of methylene on aromatic rings stretching, 1353 and 1238 due to the O–H of phenols stretching, 1094, 1071 and 1030 cm⁻¹ due to the C–O–C of ester stretching [15,46,55]. In terms of figure 2, the CS/TP-based SCLs are mainly evidenced by some

intense peaks located at 3430 contributed by both CS and TP, 2890 contributed by CS, 1587 contributed by both CS and TP due to the N–H and C–H groups of CS bonded to the aromatic C=C structure of TP. While peaks at 1383 contributed by both CS and TP are due to the C-CH₃ of CS bonded with the C–H of methylene on aromatic rings and O–H of phenols of TP, 1157 contributed by both CS and TP due to the C–O of saccharide molecules of CS bonded with the O–H of phenols and C–O–C of ester of TP, 1071 contributed by both CS and TP and 896 cm⁻¹ contributed by CS. Since these CS/TP-based SCLs presented the peak shift for peaks at 1587 and 1383 cm⁻¹, this suggested that the formation of CS/TP-based SCL was by the interactions among the N–H and C–H groups of CS with the aromatic C=C structure of TP, and the C-CH₃ of CS with the C–H of methylene on the aromatic rings and O–H of phenols of TP.

3.3 Anti-UV properties of CS/TP-based SCL

The protection against UV rays in relation to different UV protection levels have been labelled as class-1 and -2 for SCL defined by the U.S. Food and Drug Administration, FDA, and also the standard of Z80.20 by American National Standards Institute, ANSI [59]. However, these standards defined different scales. According to FDA, the class-1-based SCL should block 90% UV-A rays and 99% UV-B rays, while the class-2-based SCL should block 70% UV-A and 95% UV-B radiation. According to FDA, the class-2 blockers should fit the general environments better, and the class-1 blockers should have high exposure environments such as mountains or beaches [59].

From figure 3, left, it was clearly found that these CS/TP-based SCLs all presented good UV protection ability in full UV ranges by comparison of the pure CS-based SCL. For CS/TP-based SCL with 1% TP, the UV-C, UV-B and UV-A protection were greatly reduced at least about 54, 58 and 36%, respectively. In terms of figure 3, left, the increase of

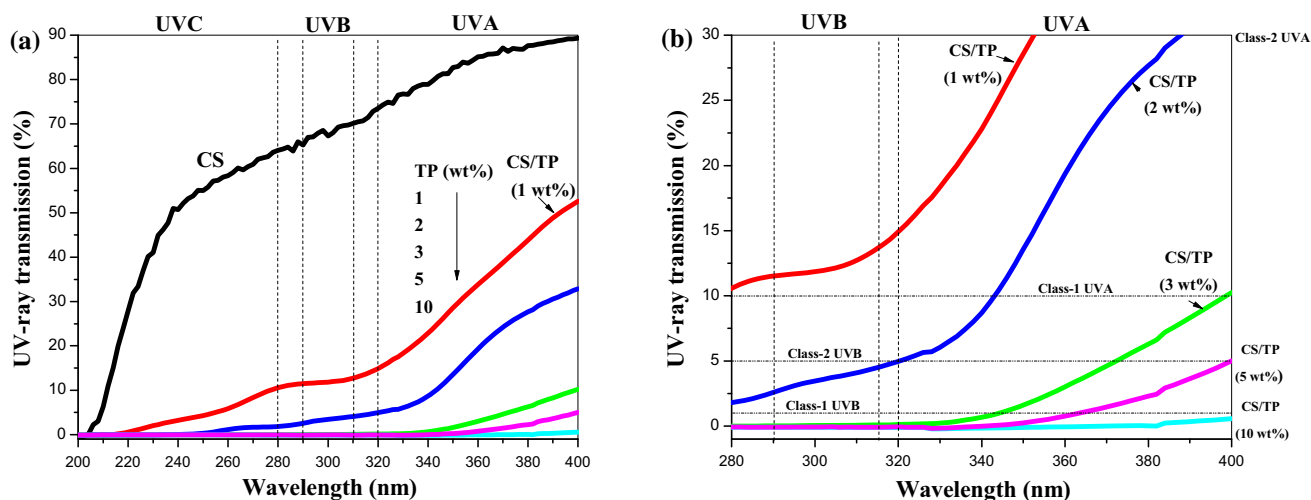


Figure 3. UV-ray transmission percentage in relation to whole UV range, e.g., from UV-A, UV-B to UV-C (a) and under FDA defined class-1 and -2 for pure CS and CS/TP-based SCL with TP at 1, 2, 3, 5 and 10 wt%, respectively (b).

the TP percent in CS/TP-based SCL can enhance the UV protection.

According to figure 3, right, the CS/TP-based SCL with 2% TP can fit the class-2 defined UV-B condition and the TP increased to about 3% can approach the class-1 defined UV-A and UV-B conditions. Moreover, the TP 3%-based CS/TP sample showed good anti-UV properties capable to compare with literature reported values for some commercial SCLs, e.g., the Acuvue Moist of Johnson & Johnson, Cooper Vision, Neolens of EuroLent, 55 YV of Ocular Science [60]. In fact, the CS/TP 3%-based SCL (figure 3, right) presented greater UV-R values are also comparable to the very recently reported PVA/graphene oxide sample, e.g., the UV-B at 97.5% [61]. Therefore, it can be concluded that the CS/TP-based SCL can present good anti-UV properties to fit the class-1 standard of FDA and compare with literature reported PVA/graphene oxide sample [61]. However, the CS/TP-based SCLs have also the self-antibacterial and -antioxidant properties [48] compared to others.

The transmission is an important parameter of SCL. For this case, the prepared CS/TP-based SCLs, the related UV-vis spectra are shown in figure 4, in relation to the TP percent varied at 1–10 wt%. It was found that these CS/TP-based anti-UV SCLs all presented required visible-light transmissions even the one with few TP, e.g., at about 1–2 wt%, both greater over 80% as known higher than that of the pure CS-based SCL at about 71% [62], not only in good agreement with literature [47] but also comparable with the results of PVA/graphene oxide samples, e.g., at about 76% [61]. This indicated that one can produce such SCLs by adding a few TP, e.g., at 1–2%.

Since CS/TP-based SCL is reasonable with good antibacterial and antioxidant abilities as known previously [46], this implied that SCL has multi-advantages as

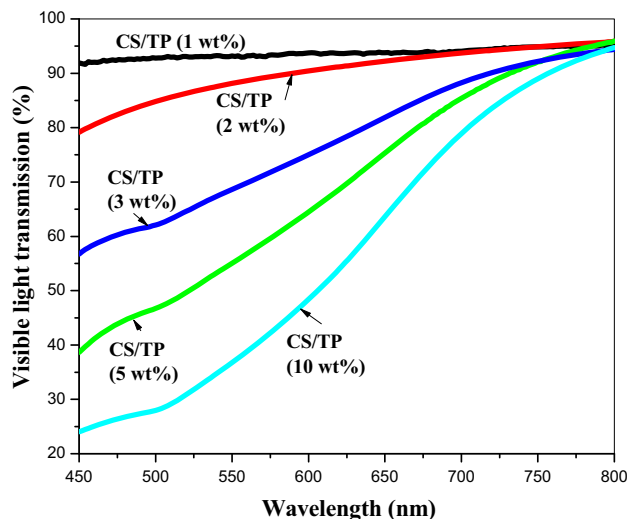


Figure 4. UV-vis spectra of the CS-based SCLs with added TP at 1, 2, 3, 5 and 10 wt%, respectively.

compared with the commercial products [60] and recently reported new sample [61].

4. Conclusions

CS/TP-based hydrogel SCL has been successfully prepared. This novel SCL presented advantages in not only the self-remained antibacterial and antioxidant properties but also the anti-UV properties fitting the class-1 standard of FDA. This CS/TP-based SCL also presented expected water content and mechanical properties to fit application standard. In terms of this work, this SCL with TP at 2% can fit the class-1 standard of FDA and at 3% can compare to the PVA/graphene oxide sample [61].

References

- [1] Ivani E J 1982 US Pat. 4365050
- [2] Allan G G 1985 US Pat. 4532267
- [3] Nicolson P C and Vogt J 2001 *Biomaterials* **22** 3273
- [4] Willcox I M D P and Holden B A 2001 *Biosci. Rep.* **21** 445
- [5] Bruce A 2003 *Cont. Lens Anterior Eye* **26** 189
- [6] Badugu R, Lakowicz J R and Geddes C D 2003 *J. Fluorescence* **13** 371
- [7] Ioannis T and Nathan E 2004 *Cont. Lens Anterior Eye* **27** 177
- [8] Gary N and Foulks M D 2006 *Am. J. Ophthalmol.* **141** 369
- [9] McCulley J P, Aronowicz J D and Uchiyama E 2006 *Dig. World Core Med. J. Ophthalmol.* **2** 17
- [10] Fonn D 2007 *Optom. Vis. Sci.* **84** 279
- [11] Boone A, Heynen M, Joyce E, Varikooty J and Jones L 2009 *Optom. Vis. Sci.* **86** 1241
- [12] Costa V P, Braga M E M, Duarte C M M, Alvarez-Lorenzo C, Concheiro A, Gil M H *et al* 2010 *J. Supercrit. Fluids* **53** 165
- [13] Yanez F, Martikainen L, Braga M E M, Alvarez-Lorenzo C, Concheiro A, Duarte C M M *et al* 2011 *Acta Biomater.* **7** 1019
- [14] Cavicchioli M, Corso C T, Coelho F, Mendes L, Saska S and Soares C P 2015 *World. J. Pharm. Pharm. Sci.* **4** 1626
- [15] Wang Y, Zhao Q and Du X 2020 *J. Mater. Chem. B.* <https://doi.org/10.1039/c9tb02389e>
- [16] Cullen A P 1995 *Health Safe* **2** 22
- [17] Philip B and Morgan N E 2006 *Cont. Lens Anterior Eye* **29** 59
- [18] Lopez C, Park S, Edwards S, Vong S, Hou S, Lee M *et al* 2019 *ACS Biomater. Sci. Eng.* **5** 1195
- [19] Deng J, Chen S, Chen J, Ding H, Deng D and Xie Z 2018 *ACS Appl. Mater. Interfaces* **10** 34611
- [20] Liu X, Chen J, Qu C, Bo G, Jiang L, Zhao H *et al* 2018 *ACS Biomater. Sci. Eng.* **4** 1568
- [21] Mak W C, Cheung K Y, Orban J, Lee C J, Turner A P F and Griffith M 2015 *ACS Appl. Mater. Interfaces* **7** 25487
- [22] *Global solar UV index: a practical guide* Geneva, Switzerland 2002 (World Health Organization)
- [23] ICNIRP (International Commission on Non-Ionizing Radiation Protection) 2004 *Health Phys.* **87** 171
- [24] Almutawa F and Buabbas H 2014 *Dermatol. Clinics* **32** 439
- [25] Yam J C and Kwok A K 2014 *Int. Ophthalmol.* **34** 383
- [26] Rosenthal F S, Bakalian A E and Taylor H R 1986 *Am. J. Public Health* **76** 1216
- [27] Bergmanson J P, Pitts D and Chu L 1987 *Acta Ophthalmol.* **65** 279
- [28] Pitts D 1990 *Optom. Vis. Sci.* **67** 435
- [29] Quesnel N M and Simonet P 1995 *Optom. Vis. Sci.* **72** 2
- [30] Lee S, Han T, Nguyen Q and Harris M 1996 *Cont. Lens Spectrum* **11** 44
- [31] Hickson-Curran S B, Nason R J, Becherer P D, Davis R A, Pfeifer J and Stiegemeier M J 1997 *Optom. Vis. Sci.* **7** 632
- [32] Tønnesen H H, Schjelderup S E and Karlsen M J 1997 *Int. Cont. Lens Clinic* **24** 123
- [33] Hermann F and Michael H Q 2000 *Clin. Article* **27** 65
- [34] Harris M G, Chin R S, Lee D S, Tarot M H and Dobkins C E 2000 *Cont. Lens Anterior Eye* **23** 10
- [35] Lopez-Alemayn A, Compan V and Refojo M F 2002 *Appl. Biomater.* **63** 319
- [36] Moore L and Ferreira J T 2006 *Cont. Lens Anterior Eye* **29** 115
- [37] DeLoss K S, Walsh J E and Bergmanson J P 2010 *Cont. Lens Anterior Eye* **33** 136
- [38] Gause S and Chauhan A 2016 *J. Mater. Chem. B* **4** 327
- [39] Berger J, Reist M, Mayer J M and Felt O 2004 *Eur. J. Pharm. Biopharm.* **57** 19
- [40] Benediktsdottir B E, Baldursson O and Masson M 2014 *J. Control Release* **173** 18
- [41] Duttagupta D S, Jadhav V M and Kadam V J 2000 *Curr. Drug Deliv.* **12** 369
- [42] Mehta P, Al-Kinani A A, Arshad M S, Singh N, van der Merwe S M, Chang M W *et al* 2019 *J. Pharm. Sci.* **108** 1540
- [43] Hoyo J, Ivanova K, Gaus E and Tzanov T 2019 *J. Colloid Interface Sci.* **543** 114
- [44] Jeenchama R, Sutteerawattananond M, Rungchang S and Tiyaboonchai W 2020 *Drug Delivery* **27** 782
- [45] Shahid-ul-Islam B S and Butola A R 2018 *Int. J. Biol. Macromol.* **120** 1999
- [46] Zhang W and Jiang W 2019 *Int. J. Biol. Macromol.* <https://doi.org/10.1016/j.ijbiomac>
- [47] Wang Y, Zhang R, Qin W, Dai J, Zhang Q, Lee K *et al* 2020 *Mater. Design* **185** 108277
- [48] Zhang L H and Shen Q 2019 *Macromol. Mater. Eng.* <https://doi.org/10.1002/mame>
- [49] Yang Q, Dou F D, Liang B R and Shen Q 2005 *Carbohydr. Polym.* **59** 205
- [50] Yang Q, Dou F D, Liang B R and Shen Q 2005 *Carbohydr. Polym.* **61** 393
- [51] Chen L, Ye J R and Shen Q 2015 *Mater. Sci. Eng. C* **56** 518
- [52] Yan Q, Wang M Y, Wu Y H, Jiang L H and Shen Q 2016 *J. Phys. Chem. B* **120** 1121
- [53] Jiang L H and Shen Q 2018 *J. Solid State Electrochem.* **22** 3311
- [54] Feng L, Li J F, Ye J R, Song W, Jia J and Shen Q 2014 *J. Appl. Polym. Sci.* **131** 40411
- [55] Wang H, Chen L, Weng L L, Zhang M Y and Shen Q 2014 *J. Adhesion Sci. Technol.* **28** 2416
- [56] Yan Q, Wang M Y, Wu Y H and Shen Q 2016 *Mater. Lett.* **170** 202
- [57] Guryca V, Hobzova R and Pradny M 2007 *Cont. Lens Anterior Eye* **30** 215
- [58] Zhu Q, Wei Y, Li C and Mao S 2018 *Mater. Sci. Eng. C* **93** 36
- [59] American Optometric Association (AOA) *UV protection with contact lenses* (<http://www.aoa.org/x12724.xml>)
- [60] Artigas J M, Navea A, Garcia-Domene M, Gene A and Artigas C 2016 *Cont. Lens Anterior Eye* **39** 141
- [61] Xie S, Zhao J, Zhang B, Wang Z, Ma H, Yu C *et al* 2015 *ACS Appl. Mater. Interfaces* **7** 17558
- [62] Anirudhan T S, Nair A S and Parvathy N J 2016 *Eur. J. Pharm. Biopharm.* **109** 61