

Ultraviolet-light-filtering behavior of fullerene–amine derivative/chitosan blended membranes

Pengfei Fang^{a,c,*}, Chaoyang Yu^b, Zhe Chen^a, Yuanyin Chen^b

^a Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China

^b Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

^c Key Laboratory of Acoustic and Photonic Materials and Devices of Ministry of Education, Wuhan University, People's Republic of China

Received 11 October 2005; received in revised form 6 April 2006; accepted 10 April 2006

Abstract

The aminated fullerene/chitosan blended membranes with novel ultraviolet-light-filtering properties have been prepared by mixing chitosan with fullerene ethylenediamine or ethanolamine derivative in a solution containing 2% acetic acid, then casting the mixture on a glass plate. The effects of fullerene-amine derivative and chitosan structures on light transmission properties of the blended membranes are investigated systematically. The fullerene derivative kind, aminated fullerene content and crosslinking degree of chitosan greatly affect their light-filtering properties, while deacetylation degree, molecular weight and carboxymethylation of chitosan only have slight influence. Further, a possible mechanism for the UV filtering property was discussed. The strong interactions, especially electron donor–acceptor occur in condensed state may play a significant role in the unique optical property.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Fullerene; Chitosan blended membrane; Ultraviolet-filtering property

1. Introduction

Fullerene materials have aroused a great deal of interest in view of their interesting photophysical and photochemical properties, such as photoconductivity, photorefractivity, optical limiting and non-linear optical property [1–5]. Every recently, Peng et al. [6] have reported that some fullerene derivatives have light-filtering property and can be able to continuously cut off lights of wavelengths almost the entire UV and visible spectral region. For example, the light transmission spectra of THF solutions of C₆₀-containing polycarbonate or poly(methyl methacrylate) continuously red shift with polymer content, their cutoff wavelengths change from near 250 to 500 nm. The similar phenomena were also observed in some aminated fullerene solutions [6]. With the rapid growth of ozone holes over the earth, the exploration of new optical materials that can cut off harmful UV radiation has attracted great interest. But for practical applications, solutions are

difficult to use and the solid-state materials (e.g. films) are demanded. However, there are a very small number of reports on solid fullerene materials with light-filtering property until now [6]. And the design of these materials still is a difficult challenge to people.

In this paper, we report a new kind of ultraviolet-filtering material: aminated fullerene/chitosan blended membranes. Chitosan is a natural, biodegradable polysaccharide derived from chitin [7]. It also has a high potential for development into sophisticated functional polymers quite different from those of synthetic polymers since it has both free amino groups and hydroxyl groups on its backbone, which are easily modified by many organic reactions, such as alkylation, carbocylation and so on. Furthermore, as a copolymer, chitosan is readily converted to fibers, films, coatings, and beads as well as powders and solutions. So the combination of fullerene with chitosan will provide more broader application possibilities, such as uvioresistant textile, optical switch, color absorber and so on. The effects of the fullerene–amine derivative and chitosan on light transmission properties of the blended membranes were investigated systematically, and a possible mechanism for the UV filtering property was proposed.

* Corresponding author. Tel.: +86 27 62552891; fax: +86 27 68753880.

E-mail address: fangpf@whu.edu.cn (P. Fang).

2. Experimental

2.1. Materials

[60]Fullerene (purity > 99.5%) was obtained from Wuhan Yin-Han 3D Carbon Cluster Hi-Tech. Co. Ltd of China. Chitosan with an average molecular weight of 1.21×10^6 and a degree of deacetylation of 78.6% was purchased from Zhejiang Yuhuan Oceanic Biochemistry Co. Ltd, China. All other reagents and solvents were AR reagents without further purification. The fullerene derivatives $H_{13}C_{60}(NHC_2H_4OH)_{13}$ and $H_{22}C_{60}(NHC_2H_4NH_2)_{22}$ were prepared as reported before [8].

2.2. Instrumentats

Light transmission spectra and absorption spectra were performed on a Shimadzu UV-1601 UV-vis spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer equipped with a 150 W Xenon source and photomultiplier tube. The fluorescence measurements were made in the wavelength of 360–700 nm at regular intervals with fixed excitation and emission slits as 10 nm. The excitation wavelength is 285 nm for $H_{22}C_{60}(NHC_2H_4NH_2)_{22}$ or 320 nm for $H_{13}C_{60}(NHC_2H_4OH)_{13}$.

2.3. Deacetylation of chitosan

Three grams of chitosan was dissolved in 100 mL of 50 wt% NaOH solution. The mixture was stirred at 85 °C for 2, 4, 8 and 24 h, respectively. Then the precipitate was collected by filtration and washed intensively with hot deionized water until neutrality. The solids were finally dried in a convection oven at 50 °C for 3 days and then in a vacuum oven at 50 °C for 12 h.

The degree of deacetylation (DD) or percentum of free amine groups in chitosan has been determined by infrared spectroscopy [9]. The chitosan powders were first dried in a vacuum oven at 50 °C until constant weight and a well-mixed mixture of chitosan and KBr at a ratio of 2:100 was made into a disc. FT-IR spectra were recorded on a Nicolet 510P spectrometer and the DD was calculated by following equation: $DD = 100 - (A_{1655}/A_{3450}) \times 115$, where A_{1655} is the peak area of the amide I band at 1655 cm^{-1} , and A_{3450} is the peak area of the OH band at 3450 cm^{-1} . The results quoted are the average values from three specimens of each sample.

2.4. Depolymerization of chitosan

Two grams of chitosan was completely dissolved in 60 mL of 2% acetic acid solution, then 25 mL of 3% H_2O_2 aqueous solution was added by drop-wise. The solution was stirred and reacted at the desired temperature (25, 40, 50, 60 °C) for 2 h. After the reaction, the solution was filtrated. The filtrate was adjusted to pH 7.0 with NaOH solution and a precipitate was obtained by adding ethanol. Low weight chitosan was collected after dried the precipitate in vacuum.

Viscometry measurement is used to determine the molecular weight of chitosan [7,10]. The viscosities of chitosan samples were measured in a solution of 0.10 M $CH_3COOH/0.25 \text{ M } CH_3COONa$ at 25 °C using an Ubbelohde capillary viscometer. The viscosity average molecular weight of chitosan was determined using the classical Mark-Houwink equation $[\eta] = 1.81 \times 10^{-3} M^{0.93}$.

2.5. O-Carboxymethylation

Three grams of chitosan was immersed in 50 mL of 50 wt% NaOH solution for 24 h. The desired amount (2, 6, 10, 15 g) of monochloroacetic acid was dissolved in 25 mL of isopropanol and then added to the solution. The mixture was stirred at room temperature for 8 h, then was filtered to remove the solvent. The filtrate obtained was dissolved in 100 mL of water, and 2.5 M HCl was added to adjust its pH to 7. After this solution was centrifuged to remove the precipitate, 400 mL of anhydrous ethanol was added to it to precipitate the product. Finally, the product was filtered, rinsed thrice with anhydrous ethanol, and vacuum-dried at room temperature.

The degree of substitution of the product was determined by using potentiometric titration [11]. The O-carboxymethylated chitosan (0.2 g) was dissolved in distilled water (40 mL). The solution was adjusted to $pH < 2$ by adding hydrochloric acid. Then, the solution was titrated with 0.1 M aqueous NaOH and the pH value of the solution was simultaneously recorded. The amount of aqueous NaOH was determined by the second order differential method. The degree of substitution (DS) can be calculated as follows [11]:

$$DS = \frac{161A}{m - 58A}$$

where $A = V_{NaOH}C_{NaOH}$, V_{NaOH} and C_{NaOH} are the volume and molarity of aqueous NaOH, respectively, m is the mass of O-carboxymethylated chitosan (g).

2.6. Membrane preparation

A series of blended chitosan membranes with various fullerene derivative contents were prepared as following procedure: A desired amount of fullerene derivative and chitosan were dissolved in 2 wt% acetic acid solution. This solution was cast on a glass plate, gradually dried at room temperature for 24 h and then removed from the plate. To neutralize the acetic acid, the membrane was immersed in a 4% NaOH aqueous solution for 10 min, and finally washed thoroughly with deionized water. A pure chitosan membrane was prepared by the same procedure for comparing.

Preparation of cross-linked chitosan or chitosan/aminated fullerene blend membranes: The chitosan solution (3 wt%) was prepared by dissolving chitosan in 2 wt% acetic acid solution (the 0.33 wt% fullerene-amine derivatives was also added for preparing blend membranes). Then a certain amount of 0.5 wt% glutaraldehyde solutions was added dropwise. After the resultant solution was stirred for 1 h, the casting method as

described previously was employed to prepare the crosslinked membranes.

3. Results and discussion

3.1. Effect of fullerene–amine derivatives on light transmission properties of blended membranes

Fig. 1 shows light transmission spectra of the pure chitosan film and fullerene ethylenediamine derivative/chitosan blended membranes. It can be seen that the blended membranes exhibit novel ultraviolet-light-filtering properties by introducing of aminated fullerene. When the content of fullerene derivative is only 0.66 wt%, the transmission spectrum of chitosan blended film (Fig. 1(b)) moves to long-wavelength region obviously relative to that of pure chitosan membrane, the transmittance of blended membrane also decrease markedly, especially in the wavelength range from 200 to 500 nm. With the aminated fullerene content continued increasing, the spectrum of chitosan blended membrane bathochromically shifts almost horizontally with little change in shape. When the content of $H_{22}C_{60}(NHC_2H_4NH_2)_{22}$ varied from 0.66 to 12.5%, the cutoff wavelength λ_c , here defined as the wavelength at which the light transmittance is 0.1%, ranges from 216 to 384 nm.

The similar ultraviolet-filtering phenomenon is also observed in the fullerene ethanolamine derivative/chitosan blended system (Fig. 2). When $H_{13}C_{60}(NHC_2H_4OH)_{13}$ content varies from 1.64 to 7.81%, the cutoff wavelength λ_c ranges from 235 to 336 nm.

As can be seen from Fig. 3, the light transmission through the fullerene derivative/chitosan blended membranes abides by the following λ_c – bc relationship [6]:

$$\lambda_c = \alpha \log(bc) + k$$

where b is the path length or film thickness; c is the fullerene derivative content of chitosan blended membrane (mg/g); α and k are constants.

It can be found that the α and k values are evidently affected by the fullerene derivatives. The α value of the chitosan/ $H_{22}C_{60}(NHC_2H_4NH_2)_{22}$ blended film is 305.7, higher than that of

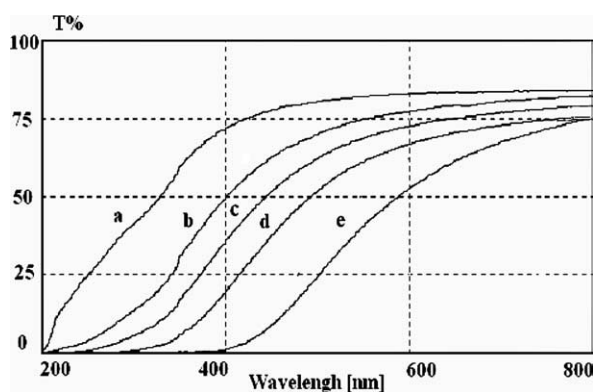


Fig. 1. Light transmission spectra of chitosan blended membranes with different $H_{22}C_{60}(NHC_2H_4NH_2)_{22}$ contents: a, 0%; b, 0.66%; c, 1.64%; d, 3.23%; e, 12.5%.

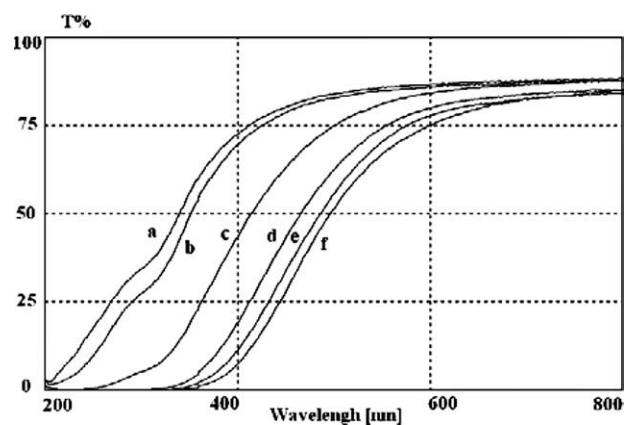


Fig. 2. Light transmission spectra of chitosan blended membranes with different $H_{13}C_{60}(NHC_2H_4OH)_{13}$ contents: a, 0%; b, 0.33%; c, 1.64%; d, 4.00%; e, 6.25%; f, 7.81%.

chitosan/ $H_{13}C_{60}(NHC_2H_4OH)_{13}$ blended membrane (282.0). And the k values are 133.5 and 149.6, respectively.

3.2. Effect of chitosan structures on light transmission property of membranes

Chitosan has both free amino groups and hydroxyl groups on its backbone, so it is easily modified by many organic reactions to improve mechanical strength, chemical stability, hydrophilicity and also biocompatibility. These chemical treatments include depolymerization, deacetylation, carboxymethylation, crosslinking and so on. Fig. 4 shows the effect of depolymerization or molecular weight of chitosan on light transmission. It was found that with the molecular weight of chitosan decreasing, the spectrum of chitosan or its blended membrane slightly shifts to long-wavelength region. It is also noted that the chitosan with low molecular weight (e.g. 7.3×10^4) has poor film forming ability when it was blended with aminated fullerene.

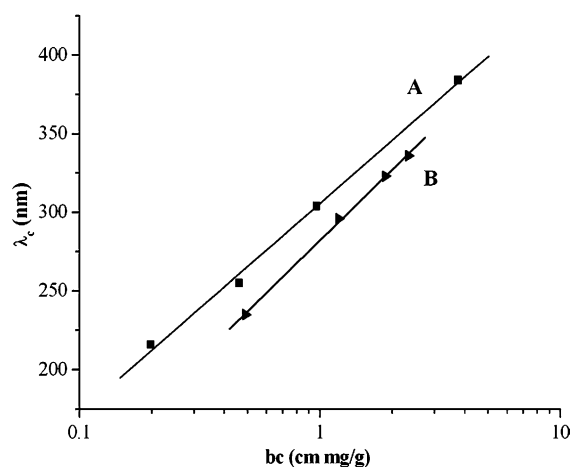


Fig. 3. Dependence of the cutoff wavelength (λ_c) on the fullerene derivative content (c) of the chitosan blended membranes with 0.3 mm thickness. A, $H_{22}C_{60}(NHC_2H_4NH_2)_{22}$ contents (mg/g): 6.6, 16.4, 32.3, 125; B, $H_{13}C_{60}(NHC_2H_4OH)_{13}$ contents (mg/g): 16.4, 40.0, 62.5, 78.1.

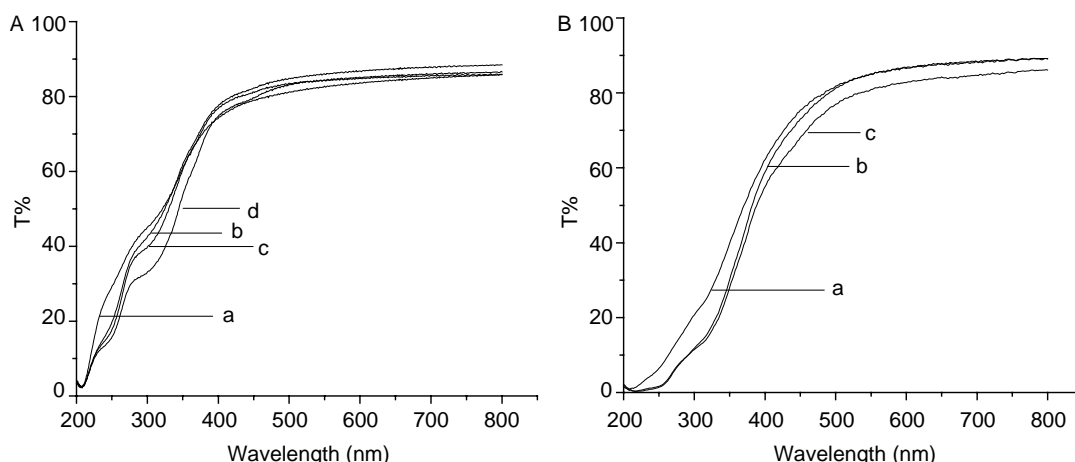


Fig. 4. Effect of molecular weight on light transmission of chitosan film (A) and chitosan/ $H_{13}C_{60}(NHC_2H_4OH)_{13}$ blend membrane (B). The molecular weight of chitosan: a, 8×10^5 ; b, 6.3×10^5 ; c, 1.4×10^5 ; d, 7.3×10^4 .

It was reported that the degree of chitosan deacetylation greatly influences the polymer's characteristics: charge density (the number of available primary amines for binding), solubility and crystallinity. The effect of DD on light transmission of chitosan and its blend membrane also was studied and showed in Fig. 5. The transmittance of pure chitosan in the ultraviolet band slightly increases with the degree of chitosan deacetylation increasing. For chitosan/fullerene derivative blend system, the DD of chitosan also has a little influence on its light transmission, but the shift of spectrum is irregular.

Chitosan with high DD is insoluble in water because of the strong intermolecular hydrogen bonding (H-bond). Nevertheless, some modifications to the OH or NH_2 positions of chitosan (e.g. carboxymethylation) could be done to improve its water solubility. *O*-carboxymethylchitosan (OCMCS) is an amphiprotic ether derivative, contains $-COOH$ groups and $-NH_2$ groups in the molecule. The light transmission spectra of OCMCS and its blend membrane are shown in Fig. 6. The spectra of *O*-carboxymethylchitosan/aminated fullerene blend membranes shift to long-wavelength region relative to that of

pure OCMCS membrane (Fig. 6(B)). However, the degree of substitution has little effect on light transmission of OCMCS or its blend films.

Crosslinking chitosan is an appropriate methodology for enhancing its mechanical properties and stability. Some crosslinking reagents have been suggested in literature, like glutaraldehyde, sulphuric acid, genipin and oxidized glucose. Glutaraldehyde is the most widely used crosslinker. Fig. 7 shows the effect of crosslinking using glutaraldehyde on light transmission of chitosan film and chitosan/ $H_{13}C_{60}(NHC_2H_4OH)_{13}$ blend membrane. It was concluded that the degree of crosslinking has distinct influence on optical property of the membranes. The transmittance of pure chitosan markedly decreases with crosslinking degree increasing especially in the wavelength range from 200 to 500 nm. The more remarkable red shift phenomenon of transmission spectra was observed in chitosan/aminated fullerene blend system. When the amount of glutaraldehyde varied from 5.30 to 26.5 mg/g chitosan, the cutoff wavelength λ_c of blend membrane ranges from 215 to about 340 nm. The results may be attributed to the formation of Schiff base when glutaraldehyde reacts with amine groups of

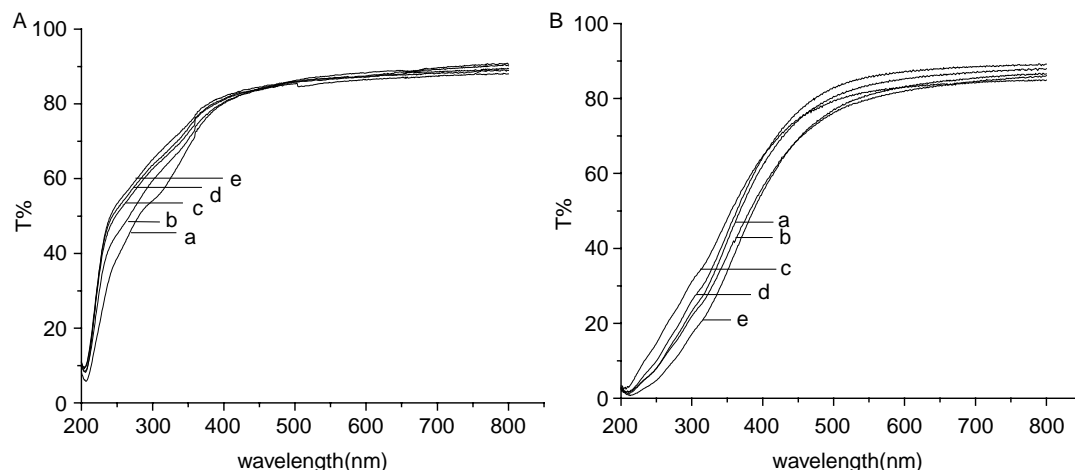


Fig. 5. Effect of the degree of deacetylation on light transmission of chitosan film (A) and chitosan/ $H_{13}C_{60}(NHC_2H_4OH)_{13}$ blend membrane (B). The degree of chitosan deacetylation: a, 85%; b, 85.6%; c, 86.1%; d, 87.5%; e, 91.7%.

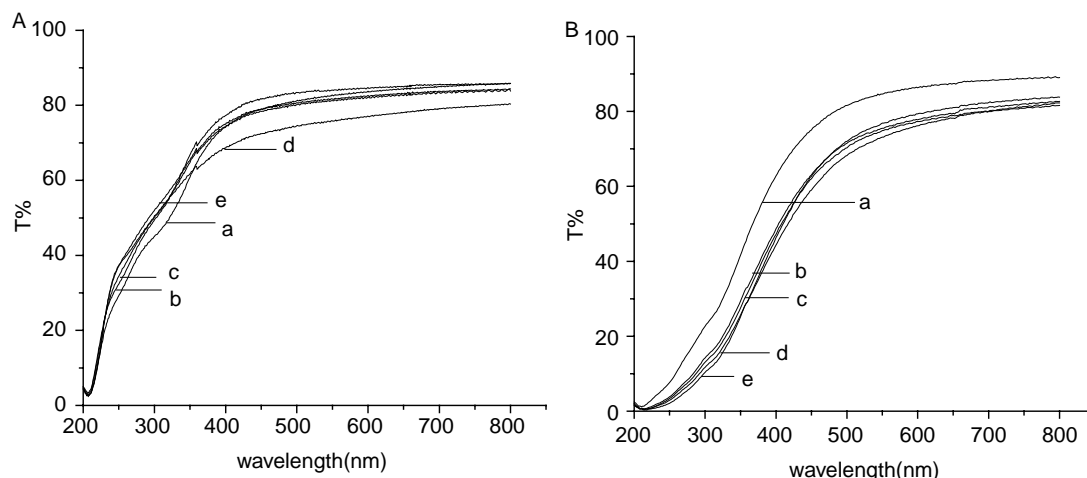


Fig. 6. Effect of substitution degree of *O*-carboxymethylated chitosan on light transmission of chitosan film (A) and chitosan/ $H_{13}C_{60}(NHC_2H_4OH)_{13}$ blend membrane (B). The degree of substitution is: a, 0; b, 0.12; c, 0.22; d, 0.43; e, 0.47.

chitosan or aminated fullerene. So the ultraviolet-filtering property also can be adjusted by controlling the crosslinking degree.

3.3. Possible mechanism for the UV filtering property

What is the cause of this novel light-filtering property? Peng et al. have reported that the fullerene molecules in solutions can aggregate into nanoclusters and suggest these nanoaggregates are responsible for the optical phenomenon. But the detailed mechanisms remained unknown in literature [6].

It is well known that there are strong interactions existing in aggregate fullerene or its derivative systems, especially in high concentration regime or condensed state. These interactions remarkably affect the material electronic and optical properties [12–21]. They maybe play a significant role in ultraviolet-filtering phenomenon. Firstly, π – π conjugate interactions is considered because C_{60} has unique three-dimensional spherical structure with delocalized π -type electrons [12–14]. To minimized disturb of other kinds of interaction, the system of

fullerene propylamine derivative/polystyrene is selected. It is believed that there are strong π – π interactions forming among fullerene molecules and between fullerene and polystyrene. Fig. 8 shows its light transmission spectra. Though the transmittance obviously decreases with fullerene derivatives content increasing in the wavelength range from 300 to 600 nm, but the distinct red shift of spectra like Figs. 1 and 2 has not been observed. In other words, the cutoff wavelength remain unchanged even though the $H_6C_{60}(NHC_2H_4CH_3)_6$ content increases to 10 wt%. The facts mean that there may be other effect factor occurring besides π – π interactions in chitosan blend systems.

On the other hand, C_{60} is a good electron acceptor and can form charge–transfer complexes (CTC) with donors such as aromatic or aliphatic amine [15–18]. And chitosan matrix and fullerene derivative in blend membrane both have strong polar groups such as amine or hydroxyl. So there are electron donor–acceptor interactions formed among fullerene amine derivatives or between aminated fullerene and chitosan. As shown in Fig. 9, with $H_{22}C_{60}(NHC_2H_4NH_2)_{22}$ concentration increasing,

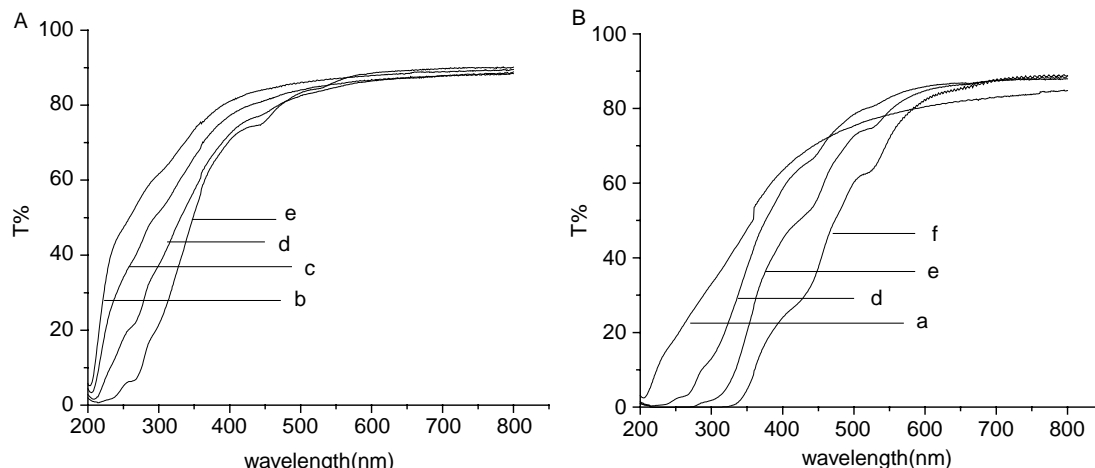


Fig. 7. Effect of cross-linking using glutaraldehyde on light transmission of chitosan film (A) and chitosan/ $H_{13}C_{60}(NHC_2H_4OH)_{13}$ blend membrane (B). The amount of glutaraldehyde (mg/g chitosan): a, 0; b, 1.06; c, 3.18; d, 5.30; e, 10.6; f, 26.5. $H_{13}C_{60}(NHC_2H_4OH)_{13}$ content of blend membrane is 0.33 wt%.

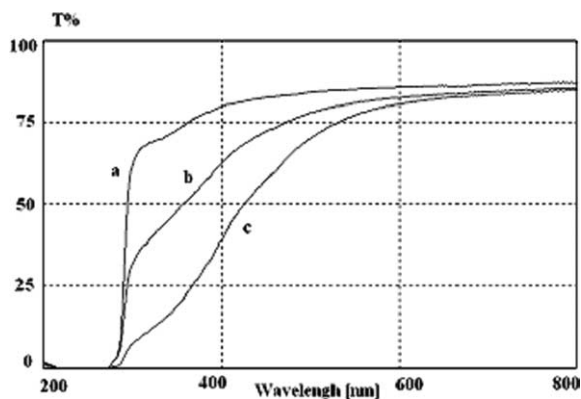


Fig. 8. Light transmission spectra of polystyrene blended membranes with different $\text{H}_6\text{C}_{60}(\text{NHC}_2\text{H}_4\text{CH}_3)_6$ contents: a, 0%; b, 3%; c, 10%.

the absorbance of solution in the wavelength range from 200 to 300 nm increases gradually, and meantime the spectrum shape also changes from two absorption peaks appearing near 192 and 218 nm to one broad and strong peak around 210 nm. In the presence of chitosan (Fig. 10), the absorbance becomes much higher, and the absorption spectra shape is very different from that in Fig. 9. And the spectra also changes with varying fullerene derivative concentrations accompanied by a red shift of the absorption band in the 200–225 nm range. These results confirm that there is interactions occurred between chitosan and aminated fullerene.

Furthermore, fluorescence quenching by aminated fullerene concentration is also observed in experiments [18,22]. Fig. 11 shows the fluorescence spectra of fullerene ethylenediamine derivative. It can be seen that the fluorescence intensity increases with fullerene derivative concentration increasing from 8.7×10^{-4} to 9.3×10^{-3} mg/mL, the maximal emission wavelength red shifts from 446 to 470 nm at the same time. When the concentration increases to 1.1×10^{-2} mg/mL, the fluorescence is quenched. For chitosan/aminated fullerene blend system (Fig. 12), the fluorescence intensity also increases with aminated fullerene concentration increasing from 3.4×10^{-3} to 4.2×10^{-2} mg/mL, the maximal emission wavelength

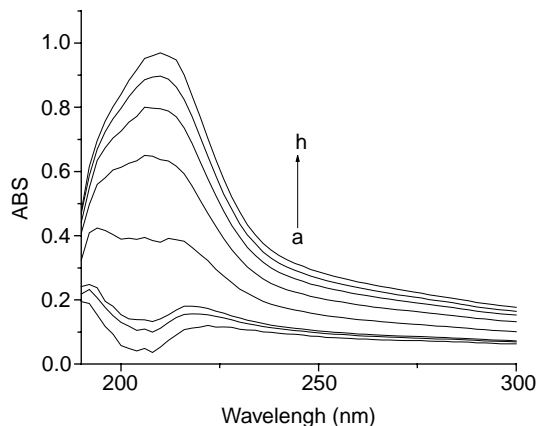


Fig. 9. Absorption spectra of fullerene ethylenediamine derivative in 2 wt% acetic acid solution. $\text{H}_{22}\text{C}_{60}(\text{NHC}_2\text{H}_4\text{NH}_2)_{22}$ concentration (a–h): 4.4×10^{-4} , 8.8×10^{-4} , 1.3×10^{-3} , 3.0×10^{-3} , 3.8×10^{-3} , 5.1×10^{-3} , 6.3×10^{-3} , 7.1×10^{-3} mg/mL.

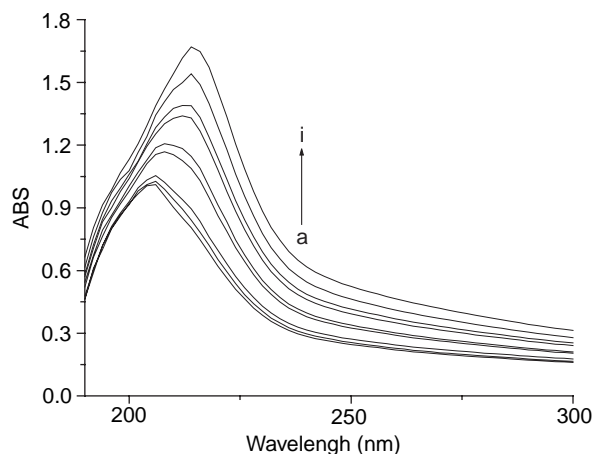


Fig. 10. Absorption spectra of fullerene ethylenediamine derivative in 2 wt% acetic acid solution in the presence of chitosan. Chitosan content: 1 wt%; $\text{H}_{22}\text{C}_{60}(\text{NHC}_2\text{H}_4\text{NH}_2)_{22}$ concentration (a–i): 5.5×10^{-4} , 1.1×10^{-3} , 1.65×10^{-3} , 2.75×10^{-3} , 3.3×10^{-3} , 4.4×10^{-3} , 4.95×10^{-3} , 6.05×10^{-3} , 7.15×10^{-3} mg/mL.

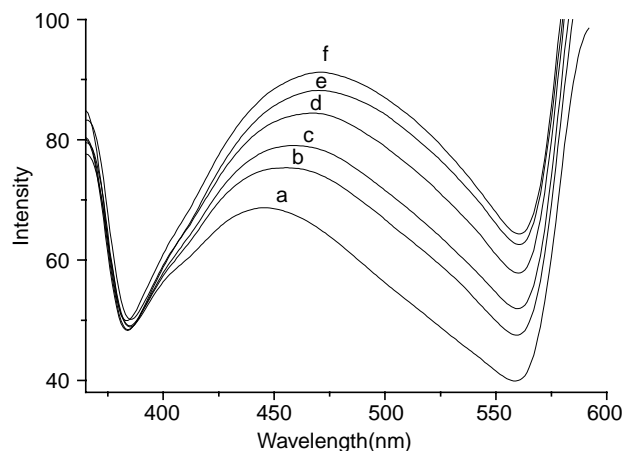


Fig. 11. Fluorescence spectra of fullerene ethylenediamine derivative in 2 wt% acetic acid solution. $\text{H}_{22}\text{C}_{60}(\text{NHC}_2\text{H}_4\text{NH}_2)_{22}$ concentration (a–f): 8.7×10^{-4} , 1.2×10^{-3} , 3.4×10^{-3} , 5.9×10^{-3} , 7.5×10^{-3} , 9.3×10^{-3} mg/mL; excitation wavelength is 285 nm.

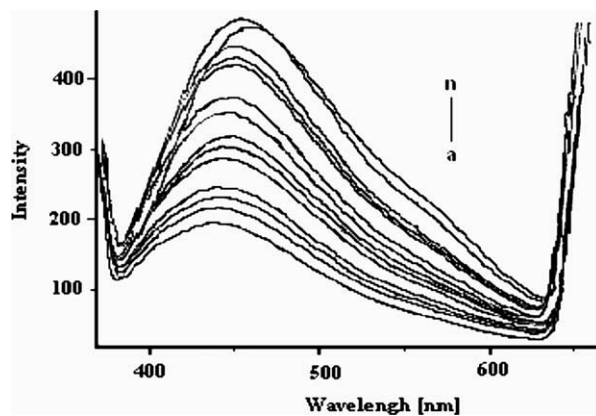


Fig. 12. Fluorescence spectra of fullerene ethylenediamine derivative in 2 wt% acetic acid solution in the presence of chitosan. $\text{H}_{22}\text{C}_{60}(\text{NHC}_2\text{H}_4\text{NH}_2)_{22}$ concentration (a–n): 3.4×10^{-3} , 4.2×10^{-3} , 4.8×10^{-3} , 5.5×10^{-3} , 8.3×10^{-3} , 9.7×10^{-3} , 1.2×10^{-2} , 1.7×10^{-2} , 1.9×10^{-2} , 2.1×10^{-2} , 2.3×10^{-2} , 2.5×10^{-2} , 4.2×10^{-2} , 5.9×10^{-2} ; excitation wavelength is 320 nm.

red shifts from 432 to 451 nm. When the concentration is higher than 6.5×10^{-2} mg/mL, the fluorescence quenching is observed. The facts also demonstrated that there are electron donor–acceptor interactions formed among the fullerene amine derivatives and between aminated fullerene and chitosan. It is also revealed that the interactions between chitosan and fullerene leave less luminescent sites available, and the inner filter effect occurs at higher concentrations [3,4,14].

These interactions, which formed among the fullerene amine derivatives and between aminated fullerene and chitosan, are suggested to exist in the condensed state [5]. They may play an important role in ultraviolet-filtering phenomenon.

4. Conclusion

In this work, the aminated fullerene/chitosan blended membranes with novel ultraviolet-light-filtering properties are revealed. With the content of fullerene derivative increasing, the transmission spectrum of chitosan blend membrane moves to long-wavelength region observably with little change in shape. And the cutoff wavelength λ_c also affected by the kind of fullerene-amine derivative introduced.

It is also found that the chitosan structures have some influence on light transmission property of blend membrane. The depolymerization and o-carboxymethylation of chitosan both bring on the slight decrease of transmittance of blend membrane. And the remarkable red shift phenomenon of transmission spectra was observed with crosslinking degree.

The absorbance of solution in the wavelength range from 200 to 300 nm increases gradually with the fullerene-amine derivative content increasing, and fluorescence quenching by aminated fullerene concentration is also observed in experiments. These facts imply that the strong interactions, especially electron donor–acceptor formed among the fullerene amine derivatives and between aminated fullerene and chitosan, may play an important role in ultraviolet-filtering phenomenon.

Acknowledgements

The financial support from the National Natural Science Foundation of China (Grant No. 20304009) is gratefully acknowledged.

References

- [1] Wang Y. *Nature* 1992;356:585–7.
- [2] Tutt L, Kost A. *Nature* 1992;356:255–6.
- [3] Sushko ML, Tenhu H, Klenin SI. *Polymer* 2002;43:2767–75.
- [4] Wang S, Xiao S, Li Y, Shi Z, Du C, Fang H, et al. *Polymer* 2002;43:2049–54.
- [5] Wang CC, Guo ZX, Fu SK, Wu W, Zhu DB. *Prog Polym Sci* 2004;29:1079–141.
- [6] Peng H, Leung FSM, Wu AX, Dong YP, Dong YQ, Yu NT, et al. *Chem Mater* 2004;16:4790–8.
- [7] Ravi K, Majeti NV. *React Funct Polym* 2000;46:1–27.
- [8] Pang DW, Zhao YD, Fang PF, Cheng JK, Chen YY, Qi YP, et al. *J Electroanal Chem* 2004;567:339–49.
- [9] Baxter A, Dillon M, Taylar KDA, Roberts GAF. *Int J Biol Macromol* 1992;14:166–9.
- [10] Tian F, Liu Y, Hu K, Zhao B. *Carbohydr Polym* 2004;57:31–7.
- [11] Ge HC, Luo DK. *Carbohydr Res* 2005;340:1351–6.
- [12] Jiang L, Sun W, Weng J, Shen Z. *Polymer* 2002;43:1563–6.
- [13] Audouin F, Renouard T, Schmaltz B, Nuffer R, Mathis C. *Polymer* 2005;46:8519–27.
- [14] Tarassova E, Aseyev V, Tenhu H, Klenin S. *Polymer* 2003;44:4863–70.
- [15] Konarev DV, Lyubovskaya RN, Drichko NV, Semkin VN, Graja A. *Chem Phys Lett* 1999;314:570–6.
- [16] Sariciftic NS, Smilowitz L, Heeger AJ, Wudl F. *Science* 1992;258:1474–6.
- [17] Stephens PW, Cox D, Lauher JW, Mihaly L, Wiley JB, Allemand P-M, et al. *Nature* 1992;355:331–2.
- [18] Qiao JL, Gong QJ, Du LM, Jin WJ. *Spectrochim Acta A* 2001;57:17–25.
- [19] Ravi P, Dai S, Hong KM, Tam KC, Gan LH. *Polymer* 2005;46:4714–21.
- [20] Song T, Dai S, Tam KC, Lee SY, Goh SH. *Polymer* 2003;44:2529–36.
- [21] Sawada H, Hata S, Kawasaki N, Iidzuka J, Tokugi K, Kyokane J, et al. *Polymer* 2002;43:1035–8.
- [22] Qiu J, Yin Q, Yao GQ, Li FM. *Acta Polym Sinica* 1996;608–11.