

UV-Vis Irradiation Fatigue Resistance Improvement of Azo Photochromic Compound Using Polyurethane-Chitosan Double Shell Encapsulation

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ABSTRACT: Double shell photochromic microcapsules were prepared by in situ polymerization with polyurethane and chitosan as inner and outer shell respectively. FT-IR indicated that chitosan-glutaraldehyde copolymer formed by imine and combined with polyurethane photochromic nanocapsules. The polyurethane-chitosan microcapsules exhibited a near-spherical shape, and the average particle size of nanocapsules was around 1.2 μm . The half-life of azo compound increased from 135 to 340 min after encapsulated in polyurethane-chitosan microcapsules. The polyurethane-chitosan shell delayed the coloration process for 14 s compared with azo compound in ethanol, however, the absorbance of azo compound increased by 17.15% in polyurethane-chitosan microcapsules. It decreased from 0.3486 to 0.1738 in ethanol during 20 s, however, it decreased from 0.4084 to 0.2625 in polyurethane-chitosan microcapsules in 55 s when it reached steady state during decoloration process. Polyurethane-chitosan double shell encapsulation is an effective route for improving the fatigue resistance, increasing the absorbance of azo compound. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40895.

KEYWORDS: degradation; kinetics; light scattering; optical properties; polyurethanes

Received 29 January 2014; accepted 17 April 2014

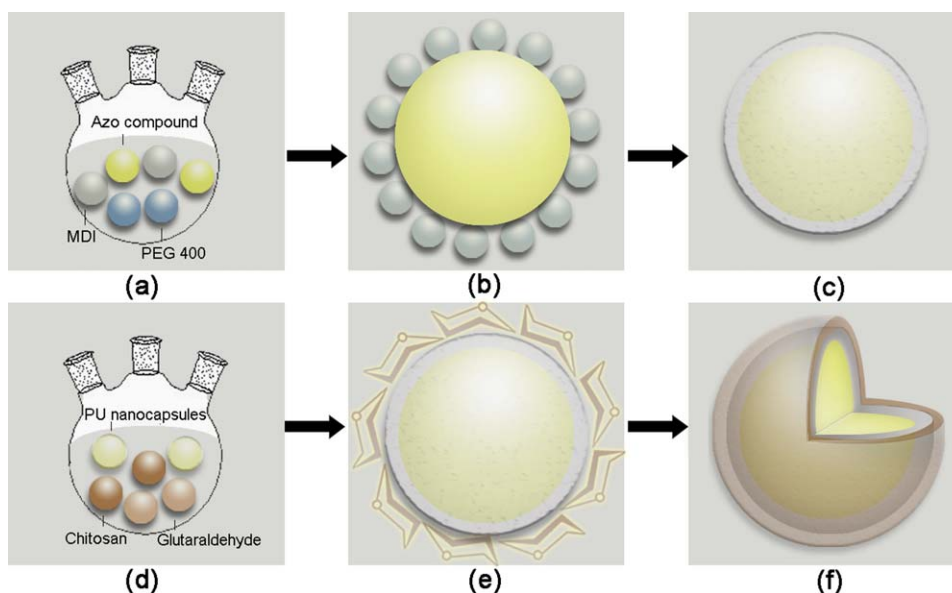
DOI: 10.1002/app.40895

INTRODUCTION

Photochromic compound often can instantly change absorption spectral and exhibit bright color,^{1,2} however, it is susceptible to be affected by the environmental factors such as pH,² oxidation, light, and temperature which lead to poor photochemical fatigue and deterioration after numerous repetitive cycles of irradiations.^{3–5} Moreover, irradiation intensity and time also have an influence on fatigue resistance. Encapsulated photochromic dyes can dissolve the resulting poor fatigue resistance problems.^{6–8} Oily photochromic pigment dissolved in some solvents brings about different types of interactions between surrounding medium and azo compound which can result in a change in the position, intensity and shape of absorption bands.^{9–11} Double encapsulation is able to further increase the clad ratio of photochromic pigment, resulting in increased leakproofness of the photochromic microcapsules. Moreover, the increased surface reflection, interface reflection, and refraction make scattering increased and the irradiation intensity weakened.

The leakproofness correlates well with the wall structure. The higher leakage of the microcapsules might be the result of their lower degree of completeness of the wall.¹² The half-life of spi-

rooxazine in poly(methyl methacrylate) and ethyl cellulose nanocapsules prepared via emulsion-solvent evaporation were improved to 300 min and 290 min respectively, compared to 170 min for spirooxazine dissolved in acetonitrile.¹³ The leakproofness for the microcapsules increases with the layer number and the initial burst phenomenon is relieved after encapsulation, owing to the increase in multilayer thickness.¹⁴ Double shell microspheres present a promising route for control of leakproofness by varying the degradation rate, erosion mechanism of the polymer used as wall material or the thickness of the shell.¹⁵ It indicated that increasing the ripened wall thickness and compactness is a more effective way of preventing the material leakage than further increasing the thickness of the unripened wall.¹⁶ Double shell polymer structure can be prepared via various approaches to obtain required properties. One method is to encapsulate active substance in microparticles by conventional microencapsulation method and then coat the particles with a second polymer. With the outer coating, the active substance diffusion and the burst effect during the process are reduced because no active substance is entrapped on the surface of the particles.⁵ Double encapsulation with complete ripened wall material and good transmittance is profit for increasing the



Scheme 1. Schematic diagram of the formation of the double shell microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

leakproofness of photochromic compound according to above researches.

The characteristics of polyurethane are high tensile, chemical resistance, good processability, good thermoplastic, elastomeric, thermoset, linear and crosslinked mechanical properties.^{17,18} Chitosan is non-toxic, film forming capacity and high tensile strength, has been used as a matrix to encapsulate some drugs in the pharmaceutical industry.^{19,20} It is easy biodegradable and of good biocompatibility;²¹ chitosan microcapsules formed with uniform morphology, controllable outer surface²² and adjustable leakproofness.²³ Furthermore, the absorption spectra of polyurethane and chitosan is different from that azo compound need to change color, it means that polyurethane and chitosan as wall material have no influence on the absorption spectra of photochromic azo compound.

Photochromic properties and photochemical fatigue resistance after numerous repetitive cycles of irradiations are two essential parameters of photochromic compound in most of applications. The aim of this work is to prepare micro-scaled, near-spherical shape photochromic microcapsules with good compactness and transparency. Polyurethane and chitosan are applied as inner and outer wall material respectively via in situ polymerization, which have been designed for increasing the clad ratio and leakproofness, furthermore, to improve the fatigue resistance after numerous repetitive cycles of irradiations and the absorbance of the applied photochromic compound when it reaches to steady state. During this research, the photosensitive kinetics of both azo compound and the polyurethane-chitosan microcapsules were studied. We investigated the morphologies of polyurethane-chitosan microcapsules by TEM and SEM. The resultant microcapsules were characterized by FTIR, and color change properties were measured and characterized by UV-Vis light to simulate sunlight. Fatigue resistance was characterized by half-life and times of reversible coloration or cycle life.

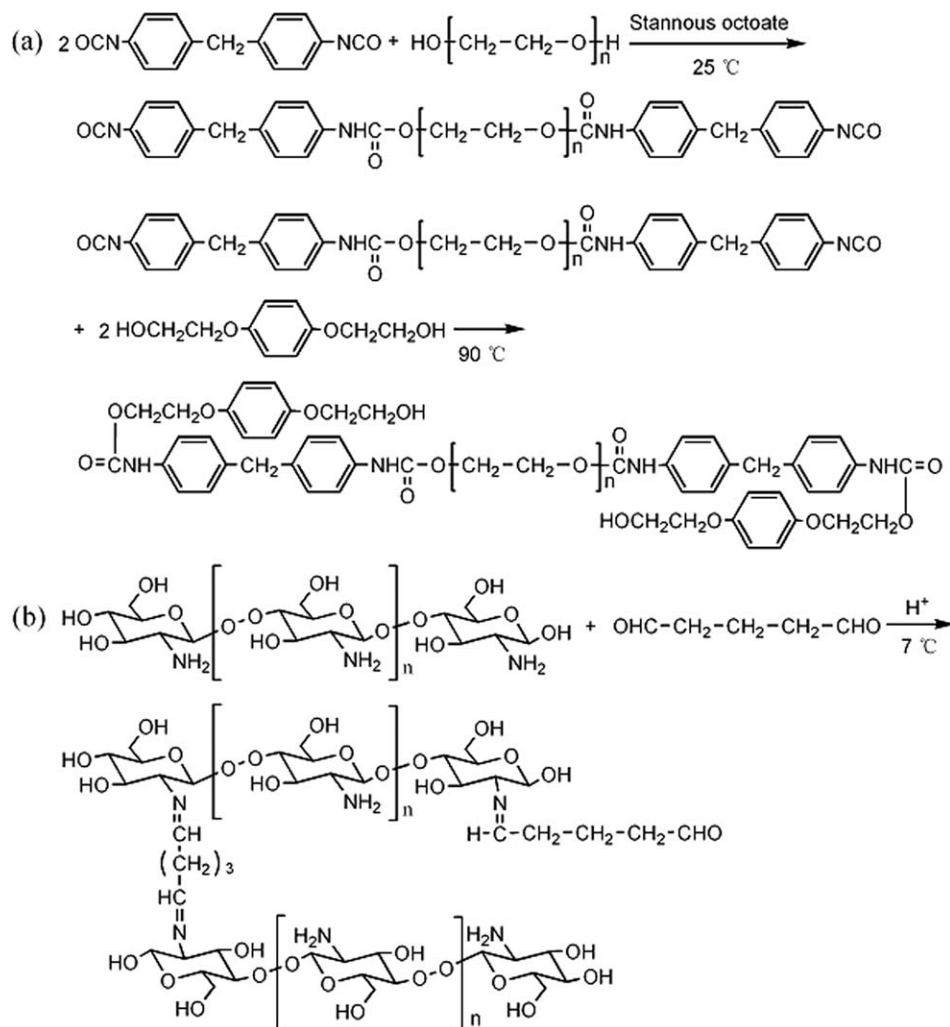
EXPERIMENTAL

Materials

1-(4'-N,N-Dimethylamine benzene azo) anthraquinone used as photochromophore, was obtained from Shenzhen Bianse Chemical Technology Co., Ltd. (AR, Shenzhen, China). Polyethylene glycol 400 (PEG400), stannous octoate, 1,3-butanediol, and anhydrous ethanol were provided by Sinopharm Chemical Reagent Co. (all AR grade, Shanghai, China). While both 4,4'-diphenylmethane diisocyanate (MDI) and hydroquinone *bis*(2-hydroxyethyl) ether (HQEE) were available from Tokyo Chemical Industry Co. (all AR grade, Tokyo, Japan). Chitosan, with 8.5×10^5 , 12×10^5 , 15×10^5 molecular weight (MW) respectively and corresponding 90%, 85%, and 80% degree of deacetylation for microcapsule wall materials were purchased from Sigma Chemical Co. (all BR grade, St. Louis). Glutaraldehyde (25%, aqueous solution, AR), liquid paraffin (CP), butyl acetate (AR), citric acid (AR), Tween 80 (AR), acetone (AR), isopropyl alcohol (AR) and petroleum ether (AR) were provided by Sinopharm Chemical Reagent Co. (Shanghai, China).

Preparation of Polyurethane-Chitosan Double Shell Photochromic Microcapsules

The procedures of preparing polyurethane-chitosan double shell microcapsules are presented in Scheme 1, (a) azo compound was surrounded by polymerization monomer, (b) prepolymer accumulated on the surface of azo compound gradually, (c) ripened polyurethane nanocapsules (PUNC) formed, (d) PUNC was emulsified into chitosan aqueous solution, then dispersed into liquid paraffin solution, (e) the chitosan-glutaraldehyde copolymer accumulated on the surface of PUNC bit by bit, (f) PUNC was wrapped up by ripened chitosan. Synthesis route of polyurethane-chitosan double shell photochromic microcapsules is shown in Scheme 2. Polyurethane nanocapsules were synthesized by referencing some earlier reported procedures.^{24–26}



Scheme 2. Synthesis route of polyurethane photochromic nanocapsules (a) and polyurethane-chitosan double shell microcapsules (b).

Polyurethane nanocapsules containing azo compound with polyurethane as wall material were prepared via *in situ* polymerization. Azo compound was stirred to dissolve in 50 mL butyl acetate and homogenized before they were poured into three-neck flask. Then 0.2 g MDI, 0.16 g PEG 400, 0.025 g Peregol O used as emulsifier and 0.003 g stannous octoate were added and then stirred to dissolve in the 50 mL butyl acetate in the same flask in sequence at room temperature for 2 h to initiate the *in situ* polymerization to obtain polyurethane prepolymer. Finally, 0.035 g HQEE and 0.012 g 1,3-butanediol were added into the prepolymerization solution to conduct the chain extension reaction at 90°C for 15 min and polyurethane wall material formed. The prepared nanocapsules were then separated by centrifugation, washed seven times, twice with acetone, twice with a 30% ethanol, and three times with anhydrous ethanol, followed by further centrifuging and vacuum-drying at room temperature, and then stored in a desiccator until used.

Microencapsulation of polyurethane-chitosan photochromic microcapsules were also carried out through *in situ* polymerization. Preparation of polyurethane-chitosan photochromic micro-

capsules was carried out by following a modification of an earlier reported procedure.²⁷ Chitosan (1.0% w/v) was dissolved in 20 mL of 2.0% w/v aqueous citric acid solution until the solution was transparent. According to 1:4 core/wall weight ratio, 0.5 g PUNC was dispersed in 10 mL deionised water with Tween 80 (5% w/v) as an emulsifier, followed by homogenized and added to the chitosan solution. The mixture was then dispersed into 100 mL of solution containing liquid paraffin containing 5% w/v Tween 80 at a constant temperature of 50°C . The mixture was then agitated using polytetrafluoroethylene stirrer with a half moon paddle for 20 min at speed of 1100 rpm. After that, the mixture was cooled below 7°C in ice bath. Crosslinking agent of 1 mL glutaraldehyde (25%, water solution) was further added dropwise to the cooled mixture, then the chitosan-glutaraldehyde copolymer accumulated on the polyurethane nanocapsules surface bit by bit and wrapped up PUNC, and stirred for another 90 min to stabilise the microcapsules through crosslinking reaction. The microcapsules products were obtained by centrifugal separation, rinsed repeatedly with isopropyl alcohol and petroleum ether to remove residual surfactant and monomers. Finally, the microcapsules were spray-dried in a Spray Drier (Yamato ADL311, Japan)

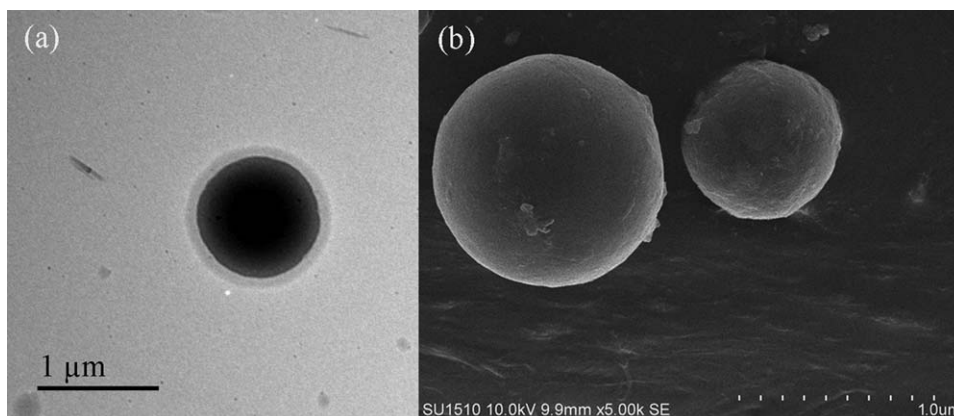


Figure 1. TEM image of polyurethane-chitosan photochromic microcapsules including 14 wt % azo compound (a), SEM image of polyurethane-chitosan photochromic microcapsules including 14 wt % azo compound (b).

through a nozzle of 406 μm . The process conditions were: inlet temperature 110°C, pressure at 0.1 MPa, drying air amount 0.1 cm^3/min , feed rate 2.6 mL/min , Outlet temperature was 70°C, respectively and then stored in a desiccator until used.

Characterization

Characterization of Polyurethane-Chitosan Photochromic Microcapsules. The formed microcapsules were characterized by an FT-IR on NICOLET is10 transform infrared instrument (Thermo Fisher Scientific, China Co. Ltd.) using KBr disks. The size of photochromic microcapsules were measured on a Nano-ZS90 Nano Particle Size and Zeta potential Analyzer (Malvern Instruments Ltd., Britain). The average particle size was expressed according to intensity.

The surface morphology and size of photochromic microcapsules were measured at room temperature on a Hitachi SU1510 scanning electron microscope (Hitachi, Ltd., Japan). The microcapsules were mounted on a support platform, air dried and fixed on an aluminum stub with a conductive copper tape, and then covered with a gold layer (99.9% purity) with a Sputter Coater (JFC-1100, JEOL, Japan).

The microcapsules were dispersed in anhydrous ethanol, then dropped onto carbon-coated copper grid, and dried under room temperature, after that, the morphology and structure of microcapsules were examined with transmission electron microscope (TEM) using a JEM-2100 electron microscope (Japan Electron Optics Laboratory Co., Ltd.).

Transparency of polyurethane films, chitosan films as well as polyurethane-chitosan double layer films was measured according to the transmittance of films that are of the same thickness like the formed shells of microcapsules, using a UV-2802S UV-Vis spectrometer (Unico Instrument Co., Ltd., Shanghai, China). Film specimens were cut into rectangles (0.7 \times 2.0 cm) and placed in the quartz spectrophotometer cell.²⁸ The relative transparency was measured by transmittance (%) at 200 nm to 500 nm.

Characterization of Light-Responsive Properties. Photographs were taken in order to monitor the coloration and decoloration processes of azo compound solution and polyurethane-chitosan photochromic microcapsules dispersion (azo compound

concentration was 10 wt %) under sunshine irradiation for 1 min. The azo photochromic compound was dissolved in ethanol and the photochromic polyurethane-chitosan microcapsules were dispersed in ethanol (azo compound concentration was 10 wt %). The photographs of coloration and decoloration processes of azo compound solution and photochromic microcapsules suspension were taken by a camera of Canon EOS400D, the photographs were taken continuously at the intervals of 0.4 s.

The UV-Vis absorption spectra of the azo compound and the suspension of Polyurethane-chitosan microcapsules were monitored on a Cary50 UV-Vis spectrometer (Roachelab Co., Ltd., Shanghai, China) after irradiated by a medium-pressure mercury lamp (Philips Lights Corporation, 125 W) with a band filter (max. 336 nm) for 1 min.

The photochromic kinetics were monitored on the Cary50 UV-Vis spectrometer after irradiation for increasing time of arithmetic sequence, using the medium-pressure mercury lamp (Philips Lights Corporation, 125 W) in a right angle setup.

Fatigue resistance of photochromic systems was studied under continuous irradiation for many hours using a 150 W Osram XBO xenon lamp with a UG1 band filter (transmission maximum at 357 nm, UVA enhanced), while the absorbance at λ_{max} (660 nm) was monitored and recorded with the Cary50 UV-Vis spectrometer after predetermined time intervals till the absorbance fell to the minima.

RESULTS AND DISCUSSION

Morphology and Size Distribution of the Double Shell Microcapsules

Figure 1(a) displays the TEM image of the polyurethane-chitosan photochromic microcapsules fabricated in the condition of the core weight ratio at 14%. The structure of the microcapsules presents composite layers, similar to those of an onion. The dark circle stands for the polyurethane wall of microcapsules; the outer light circle stands for the chitosan wall outside; and the dark gray section in the center represents the core of microcapsules. It is clear that the prepared microcapsules show a near-spherical shape. The average particle size of polyurethane-chitosan microcapsules is about 1.2 μm and is consistent with the dynamic light scattering investigations

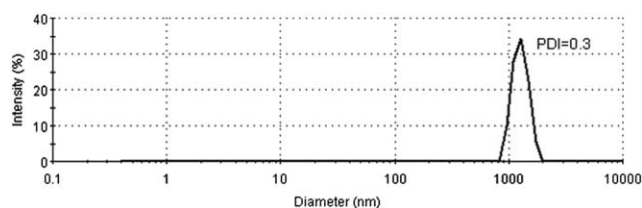


Figure 2. Size distribution of polyurethane-chitosan photochromic microcapsules including 14 wt % azo compound.

(Figure 2). The PDI value of the polyurethane-chitosan microcapsules is 0.3.

The surface morphology of microcapsules is shown in Figure 1(b). The microcapsules have a relatively smooth outer wall, and the surface morphology is with good compactness [Figure 1(b)]. The shell thickness allows the microcapsules to avoid the leakage of core material and diffusion of surrounding media toward the inside of the microcapsules, and can provide sufficient mechanical strength to prevent the microcapsules from breaking apart during processing or after inclusion into a polyurethane-chitosan carrier.

FT-IR Spectra of Polyurethane-Chitosan Double Shell Photochromic Microcapsules

The FTIR spectra of the original chitosan and polyurethane-chitosan photochromic microcapsules are shown in Figure 3(a,b), respectively. Figure 3(a) presents the principal spectra character of chitosan: 1081 cm^{-1} is related to O–C stretch; 1153 cm^{-1} is bridge–O stretch; $1313\text{--}1481\text{ cm}^{-1}$ is attributed to –CH bend; 1617 cm^{-1} is C=O stretch; 2919 cm^{-1} is attributed to C–H stretch; 3431 cm^{-1} is related to O–H stretch.^{29–31} The –NH₂ stretching vibration appears from $3500\text{ to }3420\text{ cm}^{-1}$.³² The spectrum of chitosan showed an amide characteristic peak at 1636 cm^{-1} , a broad band at 3341 cm^{-1} assigned to NH bending and two bands at 2915 and 2873 cm^{-1} assigned to CH aliphatic stretching vibrations.^{33,34} The FT-IR spectra of polyurethane-chitosan photochromic microcapsules [Figure 3(b)], absorption peaks at 1647 cm^{-1} and 1540 cm^{-1} are related to –NH–COO– stretching vibration of enclosed type isocyanate, which are attributed to the reaction between isocyanate and compound containing weak active hydrogen atom and carbamate. The characteristic peaks at 2872 cm^{-1} , and 1224 cm^{-1} represent the existences of –NH– and C–O stretching vibration or –OH deformation vibration of polyurethane, respectively. Wide absorption in $1150\text{ to }1060\text{ cm}^{-1}$ represents the vibration of C–O–C ether chain.³⁵ It shows partial disappearance of the broad peak of –NH₂ that has been found in original chitosan spectrum [Figure 3(a)]. Absorption peak at 1640 cm^{-1} is related to C=N stretching vibration, which is attributed to the reaction between chitosan and glutaraldehyde. Acylamino in chitosan matrix shows two absorption peaks [Figure 3(a)], i.e. 1639 cm^{-1} (C=O) and 1540 cm^{-1} (N–H). However, the peaks at 1639 cm^{-1} (C=O) and 1540 cm^{-1} (N–H) [Figure 3(a)] were shifted to 1693 cm^{-1} and 1553 cm^{-1} [Figure 3(b)], respectively, indicating that an interaction occurred at the amine group of the chitosan.³⁶ In addition, during the preparation of polyurethane-chitosan microcapsules, crosslinking agent was

used; the crosslinking reaction causes the peaks to shift as shown in Figure 3(a,b).

Transmittance of Polyurethane-Chitosan Shell

Maximum transmittance of polyurethane films, chitosan films as well as polyurethane-chitosan double layer films was ascribed to the surface reflection, interface reflection and refraction, as a result of refractive index of double shell material, the structure of double shell and the morphology of microcapsules. Essentially, from the TEM image of polyurethane-chitosan photochromic microcapsules including 14 wt % azo compound, it can be measured that the thickness of double shells is about 260 nm and is less than the radius of the near-spherical shape polyurethane-chitosan double shell microcapsules (600 nm), so the double shell surface can be regarded as being composed of numerous flat surfaces. The light effect mechanisms of the films are the same as microcapsules double shell. Therefore, transparency measurement of polyurethane films, chitosan films as well as polyurethane-chitosan double layer films equates to the characterization of the microcapsules shells.

Figure 4 shows the transmittance of chitosan films with different deacetylation degree, polyurethane films and polyurethane-chitosan double layer films. In the UV region (200–400 nm), at λ_{max} (260 nm) the chitosan films of 80% deacetylation degree had a maximum transmittance of 99.2%, maximum transmittance of 85% deacetylation degree chitosan films is 98.6%, and that of 90% deacetylation degree chitosan films is 97.2%. In the UV–Vis region (300–700 nm), the transmittance of chitosan films of 80% deacetylation degree is approximately 99.2% and that of 85% deacetylation degree chitosan films is around 98.6%, higher than that of the 90% deacetylation degree chitosan films (about 97.2%). Comparing the absorption peak of λ_{max} (660 nm) that azo compound solution changes color after being irradiated, the absorption peak of chitosan/glutaraldehyde

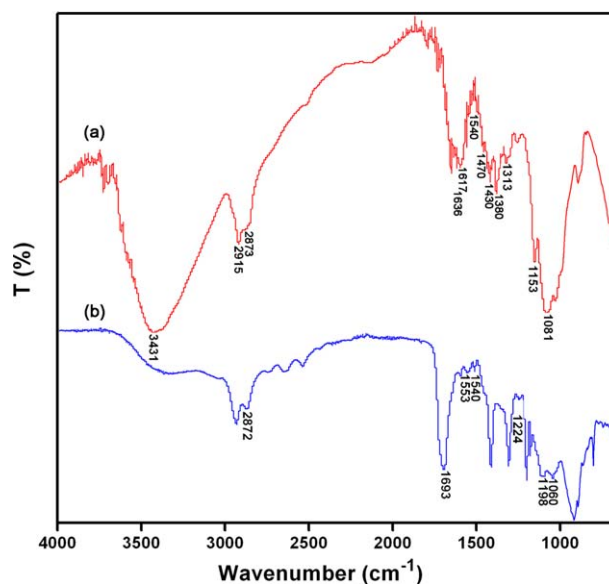


Figure 3. FT-IR spectra of (a) chitosan, (b) polyurethane-chitosan photochromic microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

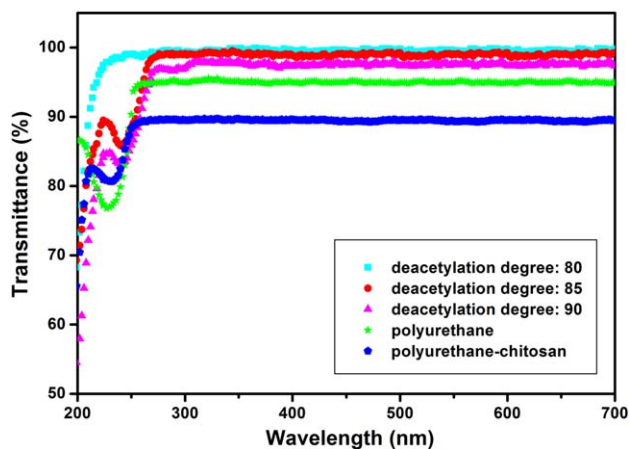


Figure 4. Transmittance of polyurethane-chitosan double layer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

film is at 256 nm. The transmittance of chitosan/glutaraldehyde film of 80% deacetylation degree is 99.2%, indicating that films of 80% deacetylation degree chitosan film have a good transmission and has no influence on the absorbance of azo compound. Finally, we chose chitosan of 80% deacetylation degree in our study to prepare microcapsules, and the polyurethane-chitosan double shells were also formed by chitosan of 80% deacetylation degree. In the UV-Vis region (200–500 nm), at λ_{\max} (260 nm) the polyurethane film has a maximum transmittance of 95.1%, and the polyurethane-chitosan film has a maxi-

imum transmittance of 89.7%. It is explained as the effect of surface reflection, interface reflection and refraction makes scattering increased, the light intensity reduced and transmittance reduced for polyurethane-chitosan double shell.

Photochromic Behavior

The azo photochromic compound was dissolved in ethanol and the photochromic polyurethane-chitosan microcapsules were dispersed in ethanol (azo compound concentration was 10 wt %), then photographs were taken at the intervals of 0.4 s to monitor the coloration and decoloration process. Figure 5 shows photographs of coloration process of azo compound solution and polyurethane-chitosan photochromic microcapsules dispersion (azo compound concentration was 10 wt %) under sunshine irradiation for 1 min. It can be observed that the azo compound solution and the dispersed photochromic polyurethane-chitosan microcapsules changed color from white to dark blue under sunshine irradiation. Moreover, azo photochromic pigment reached the steady state and increased to maximum absorbance quicker than polyurethane-chitosan double shell microcapsules.

Figure 6 shows photographs of decoloration process of azo compound solution and polyurethane-chitosan photochromic microcapsules dispersion (azo compound concentration was 10 wt %) without sunshine irradiation. The intense color of polyurethane-chitosan photochromic microcapsules changed back to the original color. Moreover, polyurethane-chitosan double shell microcapsules lost the steady state and decreased to the minimum absorbance more gradually than azo photochromic compound.

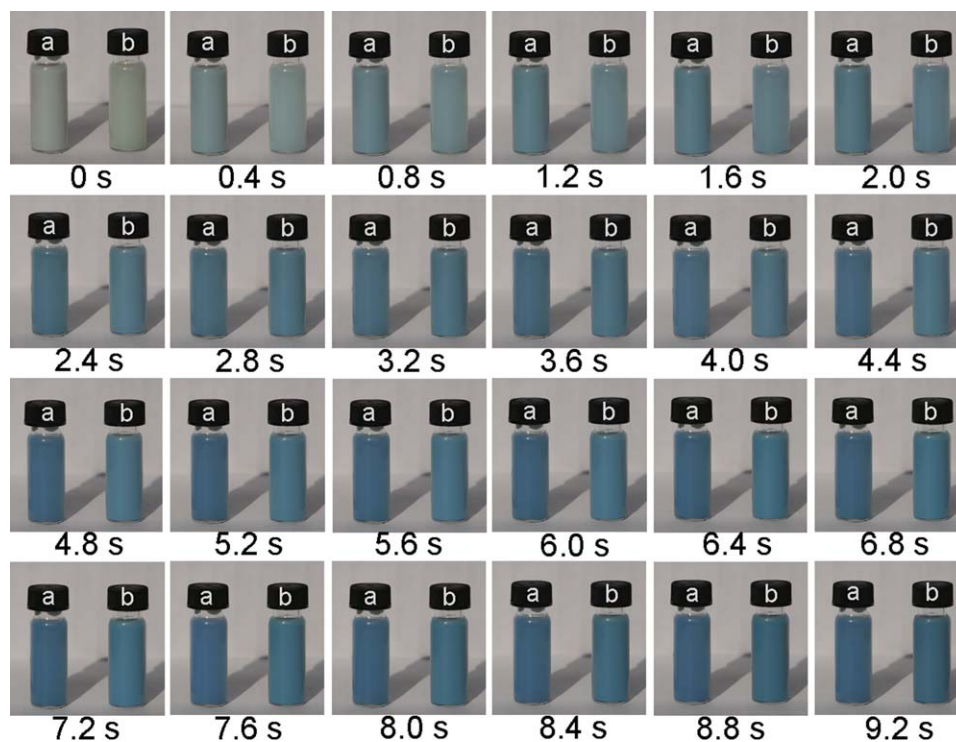


Figure 5. Photographs to monitor the coloration process of azo compound solution (a) and polyurethane-chitosan photochromic microcapsules dispersion (b) under sunshine irradiation for 1 min, azo compound concentration was 10 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

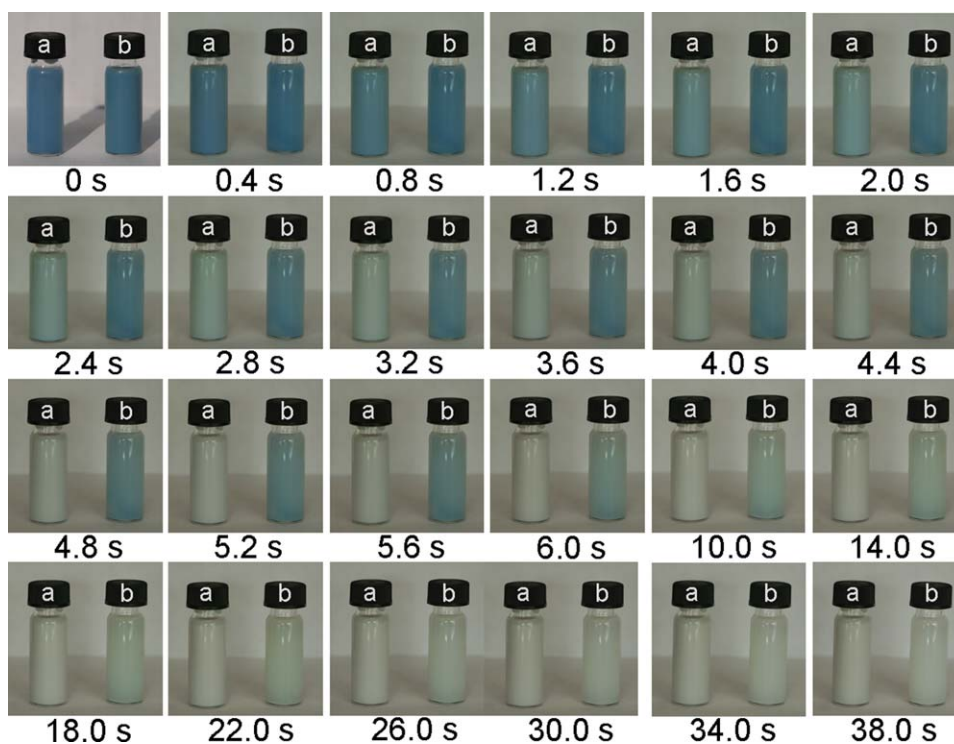


Figure 6. Photographs to monitor the decoloration process of azo compound solution (a) and polyurethane-chitosan photochromic microcapsules dispersion (b) without sunshine irradiation, azo compound concentration was 10 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The mechanism of color changes in azo compound is due to the photoisomerization of $-N=N-$ between uncolored or weakly colored meta-stable Z-isomer and the thermodynamically more stable, highly colored E-isomer under UV-Vis irradiation.^{7,38} The photoisomerization color change mechanism of azo photochromic compound is shown in Figure 7. It indicates that, in the present system, it is slower to perform the E-isomer towards the Z-isomer form as compared to the opposite process. Furthermore, this macroscopic photochemical isomerization of the polyurethane-chitosan photochromic microcapsules can be repeated reversibly for several cycles. Photochemical isomerization is defined as a reversible photo-transformation of a chemical species between two forms having different absorption spectra. During the photoisomerization, not only the absorption spectra but also various physicochemical properties change, such as the refractive index, dielectric constant, oxidation/reduction potential and geometrical structure.³⁹

The photo-sensitive microcapsules that undergo a color change upon exposure to UV-Vis light is presented in Figure 8. The spectra were taken with the polyurethane-chitosan microcapsules dispersed in ethanol (conc.: 1 % w/v azo compound) before and after UV-Vis irradiation. It can be seen that a new absorption

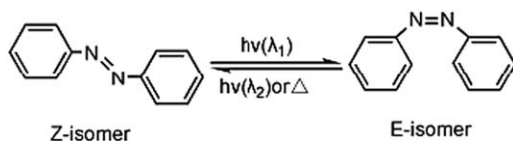


Figure 7. Photoisomerization mechanism of azo photochromic compound.

band at around 660 nm appeared due to the transformation from Z-isomer to E-isomer and presents the absorption spectrum of blue light after UV-Vis light. The photochromic microcapsules have an absorbance mainly in UV region and have an absorption peak at 235 nm before UV-Vis light irradiation.

Photochromic Kinetics of Azo Compound in Polyurethane-Chitosan Double Shell Microcapsules

Polyurethane-chitosan microcapsules have an absorption peak at 660 nm upon exciting the azo compound and polyurethane-

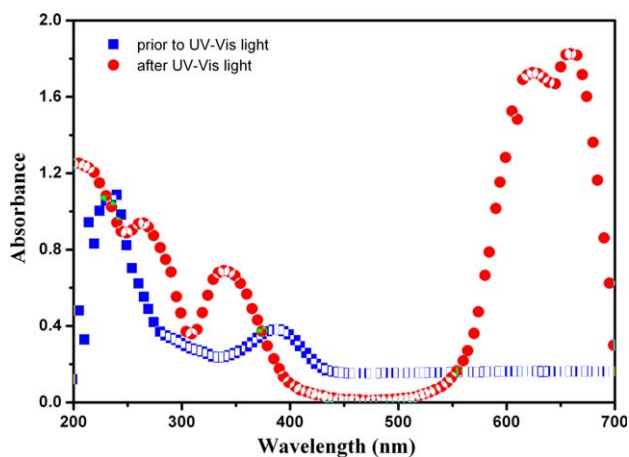


Figure 8. UV-Vis spectrum of the UV-sensitive photochromic microcapsules employed in this work prior to and after UV-Vis light exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

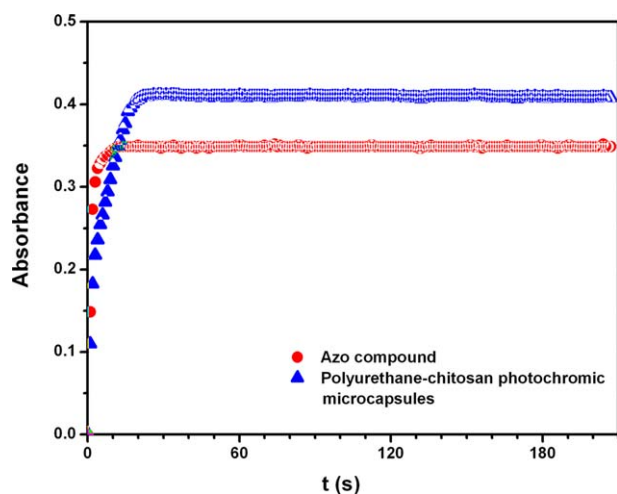


Figure 9. The absorbance changes of azo compound in polyurethane-chitosan photochromic microcapsules dispersion at the λ_{\max} (660 nm) during coloration process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chitosan microcapsules in ethanol with UV-Vis light. The coloration processes of azo compound in polyurethane-chitosan photochromic microcapsules as well as in ethanol were studied with the same azo compound concentration (containing 1 % w/v azo compound) related to the total suspensions volume. The coloration processes were illustrated in Figure 9. The absorbance of the photochromic compound increased obviously in polyurethane-chitosan microcapsules during coloration process. This can be interpreted as the azocompound was encapsulated and gathered in each microcapsules, more absorbance is the result of obviously increased concentration of azo compound in each microcapsules.

The absorbance of azo compound in ethanol was 0.3486 and it was 0.4084 in polyurethane-chitosan microcapsule during color change process, that is, the absorbance increased by 17.15%. Azo compound dissolved in ethanol reached maximum absorbance quicker than nanocapsules, that is, azo compound dissolved in ethanol reached maximum absorbance at 13 s and double shell photochromic microcapsules dispersion reached maximum absorbance at 27 s.

Transmittance of polyurethane-chitosan double shell is 89.7%, because the outer shell makes the absorbance of microcapsules moderately decreased. It can be speculated as the transmittance of polyurethane-chitosan double shell and the polyurethane-chitosan double shell structure. The absorbance of microcapsules containing azo compound decreased slightly in coloration process, since the scattering effect of double shell makes coloration depth decreased.

The rate of decoloration was explored by measuring the absorbance of microcapsule suspensions at λ_{\max} (660 nm) after a 1 min irradiation by a 125 W medium-pressure mercury lamp. The same azo compound concentration (containing 1% w/v azo compound) related to the total volume was applied in polyurethane-chitosan double shell microcapsules as well as in ethanol in these experiments for direct comparison of the decoloration processes.

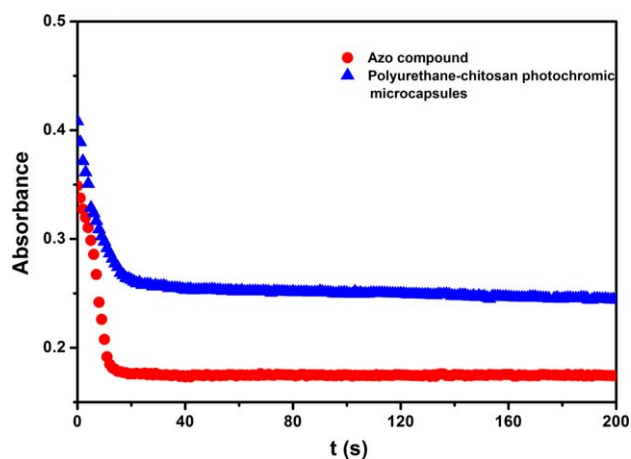


Figure 10. The absorbance changes of azo compound in polyurethane-chitosan microcapsules dispersion at the λ_{\max} (660 nm) during decoloration process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Figure 10, the decoloration rate of the polyurethane-chitosan microcapsules containing azo compound decreased significantly in the microcapsules in ethanol. The higher absorbance in microcapsules is due to the considerably decrease in the decoloration rate constant. It showed that encapsulation leads to a gradual shift in the equilibrium of the azo compound towards the isomer. Compared to the azo compound experienced in ethanol, both the coloration and the decoloration rates of the azo compound diminished in the double shell microcapsules.

In polyurethane-chitosan microcapsules, it decreased from 0.4084 to 0.2625. However, it decreased from 0.3486 to 0.1738 in ethanol in 200 s during decoloration process. Azo compound lost the steady state and decreased to the minimum absorbance at 20 s during decoloration process, for polyurethane-chitosan double shell microcapsules, it needed 55 s. It can be explained as the light and thermal storage function of polyurethane-chitosan double shell structure is better than azo compound in ethanol, and

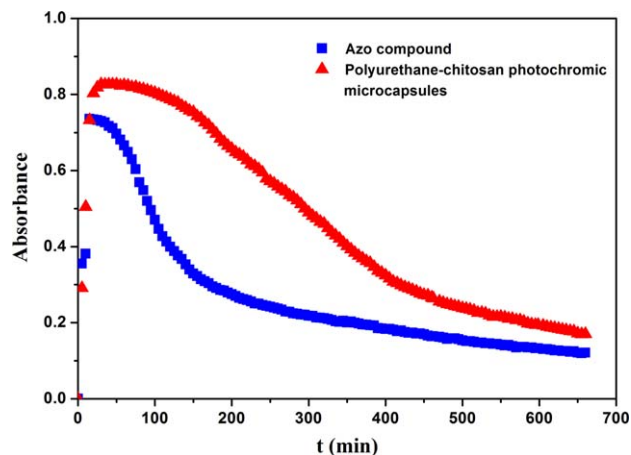


Figure 11. Fatigue of azo compound in polyurethane-chitosan microcapsules dispersed in ethanol (azo compound concentration was 1.5 wt %) upon continuous UV-Vis irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

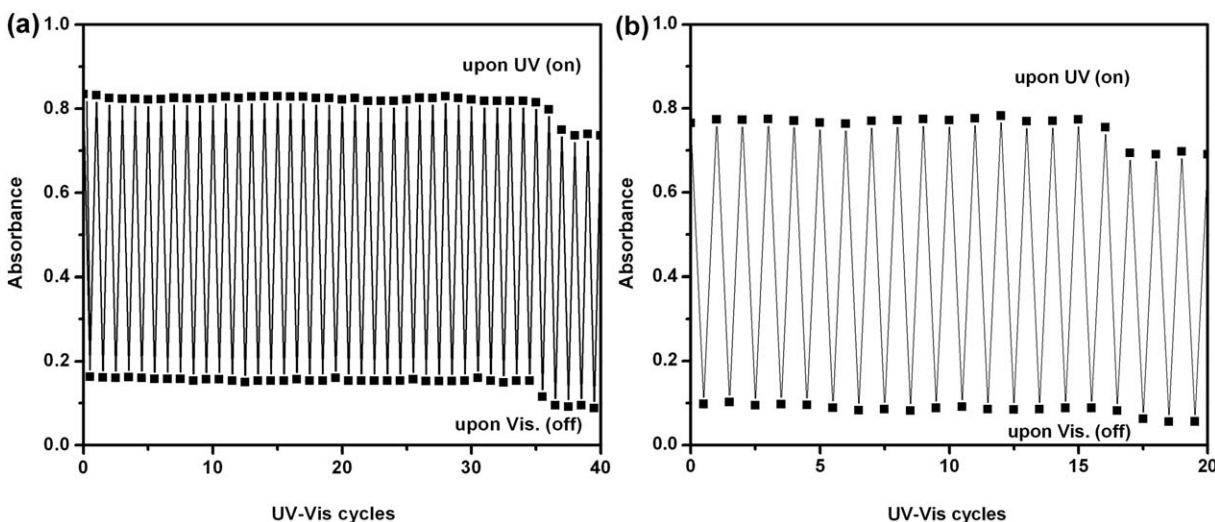


Figure 12. (a) Absorbance of polyurethane-chitosan photochromic microcapsules dispersed in ethanol upon UV (357 nm) illumination and visible light (550 nm) irradiation cycles. (b) Absorbance of azo compound dissolved in ethanol upon UV (357 nm) illumination and visible light (550 nm) irradiation cycles.

the photochromic compound shows photo-sensitive color change when light and thermal exist. Furthermore, the energy storage of double shell structure is better than single shell.

Fatigue Resistance of Capsulated Azo Photochromic Compound as Opposed to Azo Compound Solution

Azo compound solution loses the steady-state absorbance more quickly than capsulated azo photochromic compound dispersion (Figure 11). The parameter $t_{\Delta A_0/2}$ is defined as the time required for the decrease of the maximal absorbance (ΔA_0) at the λ_{\max} of the photo-isomerization form to its half value ($\Delta A_0/2$) after continuous irradiation.⁴⁰ The parameter is 135 min for azo compound solution. And the $t_{\Delta A_0/2}$ of capsulated azo photochromic compound dispersion is presented to be 340 min, which indicates the fatigue resistance of azo compound encapsulated in polyurethane-chitosan is substantially enhanced. It can be speculated as double shell structure enhances the leak-proofness of azo compound encapsulated in microcapsules and prevents the effect of oxygen, pH and other chemical agents. Additionally, it prevents the interactions between surrounding medium and azo compound which make a change in the position, intensity as well as shape of absorption bands.^{41,42} It's speculated as polyurethane-chitosan double shell can decrease the transmittance and the rate of degradation during decoloration, resulting in the increased absorbance of capsulated azo compound when the absorbance reached the steady state in color change process. Hence, the incorporation of photochromic compound in a matrix with low oxygen permeability decreases the rate of degradation.⁴³ Moreover, the increased scattering leads to weakened irradiation intensity.

Fatigue resistance as one of the important indicators of evaluating the service life of photochromic materials mainly is characterized by times of reversible coloration or cycle life. The reversible nature of the photochromic switching for the polyurethane-chitosan double shell microcapsules dispersion (azo compound concentration was 1.5 wt %) upon exposure to alternating cycles

of UV light (357 nm) and visible light (550 nm) illumination is illustrated in Figure 12, the absorption maximum of each spectrum after each irradiation was determined. The UV light and visible light can be applied to reversibly “turn on” and “turn off” the photo-response of azo compound containing microcapsules.

From Figure 12(a), it can be seen that, the incorporation of azo photochromic compound into the sealed environment can make the azo compound containing microcapsules exhibit quite good photo-reversibility, the optical switching of photo-response can be repeated for numerous times without any apparent “fatigue” effects or photobleaching until the 36th UV-Vis cycles. Moreover, compared Figure 12(a) with Figure 12(b), it is clear that cyclic photoswitching of polyurethane-chitosan photochromic microcapsules dispersed in ethanol exhibits better reversibility than that of azo compound dissolved in ethanol. We can see from Figure 12(a) that the incorporation of azo compound in the double shell microcapsules can make the microcapsules display good reversibility.

CONCLUSIONS

In this article, the polyurethane-chitosan encapsulated 1-(4'-N,N-dimethylamine benzene azo) anthraquinone microcapsules were characterized by a near-spherical shape and similar size distribution with particle size of about 1.2 μm . The half-life extended from 135 min of azo compound in ethanol to 340 min of polyurethane-chitosan microcapsules. The absorbance of polyurethane-chitosan microcapsules started to decrease at the 36th UV-Vis cycle after UV-Vis irradiation. The absorbance of azo compound reached the steady state at 13 s and was 0.3486 in ethanol, it reached the steady state at 27 s and was 0.4084 in polyurethane-chitosan microcapsules during coloration process, that is, the absorbance increased by 17.15%. Compared to the azo compound experienced in ethanol, both the coloration and the decoloration rates of the azo compound diminished in the double shell microcapsules. It decreased from 0.3486 to 0.1738 during 200 s in ethanol, and it decreased from 0.4084 to 0.2625 in polyurethane-chitosan microcapsules in

decoloration process. Azo compound lost the steady state and decreased to the minimum absorbance at 20 s, and it was 55 s for polyurethane-chitosan double shell microcapsules to reach the minimum absorbance during decoloration process. Polyurethane-chitosan double encapsulation is an effective route for improving the fatigue resistance, decreasing the rate of degradation of azo photochromic compound during decoloration process and increasing the absorbance of azo compound in applied double shell microcapsules during coloration process.

ACKNOWLEDGMENTS

The authors are grateful for the financial support of the National Natural Science Foundation of China (21174055), the Six Kinds of Outstanding Talent Foundation of Jiangsu Province (2012-XCL-007), the 333 Talent Project Foundation of Jiangsu Province (BRA2011184) and the Business Doctoral Innovation Project of Jiangsu Province in China (BK2009672).

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