

A NOVEL ANTI-MICROBIAL COLLOIDAL SILVER SYSTEM AND ITS APPLICATION FOR COSMETICS

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Summary

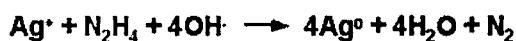
A new colloidal silver (Ag) system is present in which a fine colloidal Ag is *in situ* deposited onto functionalized porous poly (ethylene glycol dimethacrylate) (poly (EGDMA)) microspheres. The effectiveness of Ag deposition was investigated considering the surface characteristics of poly (EGDMA) microspheres. The result reported in this study illustrates that the control of surface area and surface functionality (in this study, a hydroxyl group) of poly (EGDMA) microspheres is an important factor that determines practically the degree of deposition of colloidal Ag. The x-ray analysis showed that Ag nanoparticles were dispersed evenly inner and outer surfaces and had a face center cubic (fcc) phase. In the preservative efficacy test, the Ag-containing poly (EGDMA) microspheres had a powerful anti-bacterial activity, showing a high potential for a new preservative in cosmetic industry. (**Keywords: silver, surface area, functionality, fcc phase, anti-bacterial**)

Introduction

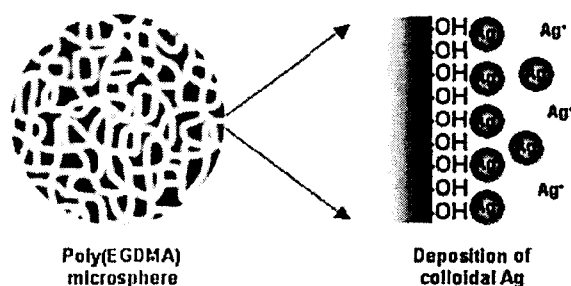
Functionalized nanocomposite materials are of great interest in the aspect of their potential applications in biomedical, electronic, and optical materials [1]. The incorporation of metal nanoparticles into polymer matrices is an area of particular interest for the study of the interaction between metal and polymer [2]. Until recently, many different methods have been proposed to obtain metal/polymer composites. Usually, metal/polymer composites were prepared by reducing metal salts in the polymer matrix or by polymerizing the matrix in the presence of metal nanoparticles [3]. However, to achieve more effective dispersion of metal nanoparticles in the polymer matrix, the blending of polymer-modified metal nanoparticles into polymer matrix has been proposed as a desirable approach [4]. This has a big advantage in that the synthetic process can be controlled easily over both metal nanoparticles and polymer matrix and applied to a variety of composite materials. Although there are many examples of metal/polymer composites as described above, there are few examples of metal/polymer colloidal system where the polymer stabilizes the

metal nanoparticles or provides a well-defined point of attachments [5].

In the present contribution, a quite different approach is proposed to produce a metal/polymer colloidal system where the colloidal Ag particles are in situ deposited onto surface characteristics-modulated polymer microsphere (Scheme 1). The polymer system we selected is poly(ethylene glycol dimethacrylate) (poly (EGDMA)) microspheres. In this study, our particular interest is concentrated on the effect of their surface area and surface functionality on the anchoring of colloidal Ag particles. The surface structure is changed successfully by controlling the network phase separation during the polymerization in the suspended monomer droplets [6]. The focus of this study is to demonstrate the importance of surface structure of polymer microspheres to get a uniform deposition of colloidal Ag particles. Consequently, the anti-microbial behavior of Ag/poly(EGDMA) microspheres was tried to construct by considering the successive oxidation/reduction reaction of Ag in aqueous media. Finally, the relationship between the anti-microbial efficacy and formulation stability were understood to overcome the limit of application of Ag in the cosmetic industry.



A chemistry of Ag synthesis



Scheme 1. A schematic presentation for the deposition of colloidal silver onto poly(EGDMA) microspheres

Materials and Method

Materials

Ethylene glycol dimethacrylate (EGDMA, Aldrich Chemical Co.), vinyl acetate (VA, Jusei Chemical Co.), silver nitrate (AgNO_3 , 99.999%, Aldrich), hydrazine (N_2H_4 , 35% in water, Aldrich), and Tween 80 (polysorbate 80, Uniquema Americas) were used as received. Polyvinyl alcohol (PVA, $M_w = 8.8 \times 10^4 \sim 9.2 \times 10^4 \text{ g mol}^{-1}$, 87~89% degree of saponification) was purchased from Kuraray Co. 2,2'-azobis(2,4-dimethyl valeronitrile) (ADV N, Wako Pure Chemicals) was recrystallized from methanol.

Preparation of poly(EGDMA) microspheres

Poly(EGDMA) microspheres were synthesized by conventional suspension polymerization, similar

to that recently reported [7]. EGDMA, VA (10wt.%, selectively in the case of incorporation of hydroxyl group), toluene, and ADVN (1 wt.% against total monomer) were mixed homogeneously and emulsified in 1 wt.% of PVA solution with a MX-5 homogenizer (Nihonseiki Co., Japan). Here, the concentration of toluene was varied to control the porosity of final microspheres as follows, 0, 20, 40 wt.% against total monomer weight. The suspension prepared was transferred to the double-walled glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. The polymerization in aqueous phase was inhibited adding a small amount of sodium nitrite (0.01 wt.%) [8]. The polymerization was carried out for 10h at 60°C at the agitation speed of 250rpm. In the case of saponification of VA in the poly(EGDMA) microspheres, 10g of microspheres produced were dispersed in methanol (100ml), and 2ml of 40% NaOH aqueous solution was added. The mixture was stirred for 5h at room temperature to yield hydroxyl-functionalized poly(EGDMA) microspheres. Then, the microspheres were recovered by filtering and repeated washing with methanol.

Deposition of colloidal Ag onto poly(EGDMA) microspheres

In Situ deposition of colloidal Ag particles onto the poly(EGDMA) microspheres was carried out by the reduction of AgNO₃ in aqueous dispersion. First, 10g of poly(EGDMA) microspheres was redispersed in 0.5 wt.% Tween 80 aqueous solution. Then, 0.3g of AgNO₃ was dissolved again in the dispersion. Then, while stirring vigorously, 5x10⁻³ wt.% of hydrazine aqueous solution was dropped slowly at room temperature. The reaction was carried out for 6h to yield a slightly dark yellow dispersion. After the reaction, Tween 80 and other unreactants were removed completely by repeated filtering with water.

Synthesis of Ag nanoparticles

Ag nanoparticles were synthesized by the reduction of AgNO₃. 0.5g of AgNO₃ was dissolved in 0.1wt% of Tween80 aqueous solution (100g). While stirring vigorously, 5x10⁻³ wt.% of hydrazine aqueous solution was dropped slowly at room temperature. The reaction was carried out for 6h. Then, surfactant and other unreactants were removed by repeated centrifuging.

Analytical characterizations

The surface and inner part images of microspheres were observed with a field-emission scanning electron microscope (JSM-6340F, JEOL). And, the silver phase in the microspheres was visualized by an energy dispersive x-ray spectrometry (EDX, Hitachi). The specific surface area, pore volume, and pore size of the microspheres were calculated from Brunauer-Emmett-Teller (BET, ASAP 2010, Micro Meritics Instrument Co.) isotherm of sorption/desorption of nitrogen. The concentration of Ag was measured with an atomic absorption spectrometer (Thermal Elemental, Solaar AAS-S4). The saponification procedure was confirmed with IR spectroscope (Nicolet, Magna IR-550) measurements. The structural state of colloidal Ag in the poly (EGDMA) microspheres was identified by the measurement of X-ray diffraction with a wide-angle X-ray diffractometer (XRD,

Bruker, Germany) in the 2 θ range. Cu K α radiation ($\lambda=1.542\text{\AA}$) was used in XRD measurements. The microscopic analysis was carried out over the time with an Optical Microscope (OM, Nikon Microphot FXA). UV-vis spectrum measurements were carried out using a Simadzu 1601 UV-Vis spectrophotometer.

Preservative efficacy test [9]

Samples were prepared by dispersing the Ag/poly(EGDMA) microspheres with the concentration in a standard oil-in-water (O/W) emulsion formulation. The recipe was summarized in Table 1. The anti-microbial efficacy of the formulations was investigated according to CTFA guideline. A mixed culture of microorganisms, *P. aeruginosa* (ATCC 9027), *S. aureus* (ATCC 6538), and *E. coli* (ATCC 8739) was obtained on TS broth after 24h incubation at 32°C. Then, 20g of samples were inoculated with 0.2g of the microorganism suspensions to adjust the initial concentration of bacteria to 10⁷ cfu/g. The inoculums were mixed homogeneously and stored at 32°C. Then, the microbial counts were carried out using the pour plate count method.

Table 1. A standard O/W emulsion formulation ^a

Component	wt. %
Stearic acid	2
Cetearyl alcohol	2
Liquid paraffin	7
Cyclomethicone	5
PEO monooleic acid ester	2
Glycerin	3
Propylene glycol	5
Triethanolamine	1
Sodium polyacrylate	0.15
Ag nanoparticles or Ag/poly(EGDMA) ^b	Variable
Water	To 100

^a Preparation process : first, oil part and water part was heated to 70°C, respectively. Continuously, the oil part was slowly added to the water part while homogenizing with the speed of 7000rpm. After another 5 min homogenizing, the emulsion produced was stabilized sterically with sodium polyacrylate. Then, the emulsion was cooled to room temperature. ^b Colloidal Ag nanoparticles or Ag/poly(EGDMA) microspheres were added changing the concentration of Ag in the emulsions.

Results and Discussion

Synthesis of functional porous poly(EGDMA) microspheres

In the field of suspension polymerization, the formation of a porous structure has been induced with the aid of network phase separation during the polymerization [6,10]. In this study, the porosity of the poly(EGDMA) microspheres was controlled by use of the above-mentioned technique. Briefly,

after the initiation, the growing EGDMA networks start to collapse by losing their solvation sheath in the monomer/solvent droplet. As the polymerization continued, the EGDMA polymer networks are separated to generate a bundle of fine inner spheres, which is responsible for the pore structure. In this process, the pore structure is influenced by the degree of crosslinking and the sort or concentration of solvent. In this study, the porosity of the poly(EGDMA) microspheres was manipulated successfully by changing the concentration of solvent.

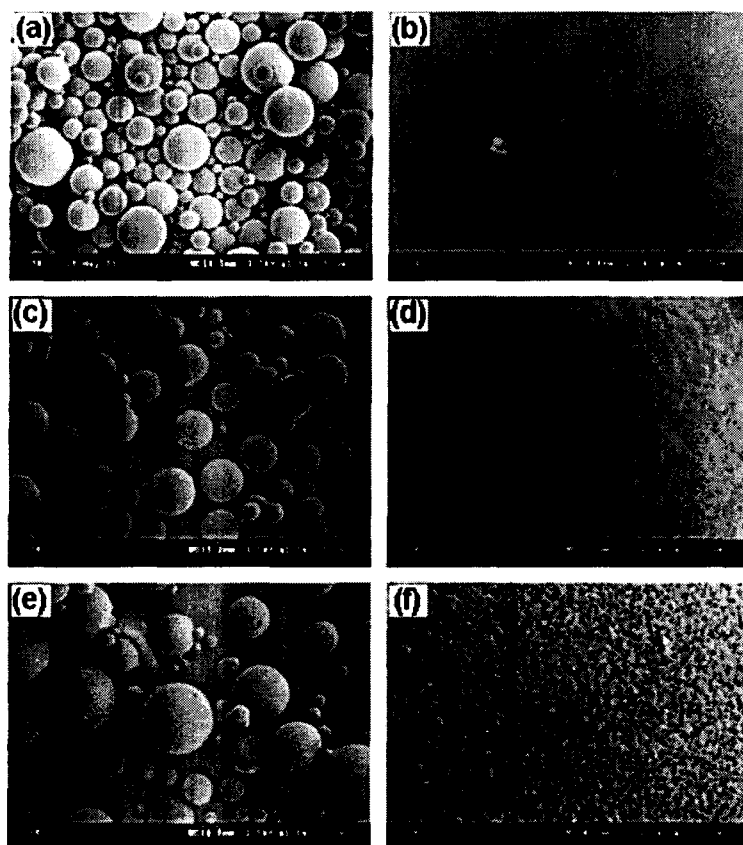


Figure 1. SEM photographs of hydroxyl-functionalized poly(EGDMA) microspheres produced with varying the concentration of solvent, toluene: (a, b) poly(EGDMA/OH)-0, (c, d) poly(EGDMA/OH)-20, (e, f) poly(EGDMA/OH)-40. The images of (b), (d), (f) show the high magnification for those of (a), (c), (e), respectively.

Figure 1 shows the SEM photographs of poly(EGDMA) microspheres with the concentration of toluene in the monomer droplets. Also, the pore characteristics measured by BET were summarized in Table 2. The SEM and BET analysis confirms experimentally that the microspheres had a different porosity depending on the concentration of toluene used. In the absence of toluene, only clear-surfaced poly(EGDMA) microspheres were formed, corresponding with typical suspension polymerization. On the other hand, in the presence of toluene, a pore structure started to appear. The porosity was enhanced as the concentration of toluene increased, which happens

because the phase separation induced by the collapse of growing EGDMA polymer networks is more favorable at low viscosity [6].

The incorporation of hydroxyl groups onto the surface of poly(EGDMA) microspheres was confirmed by IR spectroscopy measurements. From the generation of typical OH stretching vibration in the region of 3600-3000 cm^{-1} after saponification process, it is obvious that the surface of microspheres was functionalized with hydroxyl groups. In our observation, there was no evidence of morphological changes of the microspheres as a result of the incorporation of hydroxyl groups into the poly(EGDMA).

Table 2. Characteristics of Ag/polymer microspheres determined by BET and AAS

Symbol ^a	A_p ^b (m^2/g)	V_p ^c (mL/g)	D_p ^d (nm)	[Ag] ^e (ppm)
Poly (EGDMA/OH)-0	5.4	3.9×10^{-3}	2.3	undetectable
Poly (EGDMA/OH)-20	34.9	5.0×10^{-2}	5.7	2.2×10^3 (1.2×10^2)
Poly (EGDMA/OH)-40	158.3	0.40	10.1	2.7×10^3 (2.6×10^3)

^a Poly (EGDMA/OH)- α ; α is the concentration of toluene (wt.%) in the preparation of hydroxyl-functionalized poly (EGDMA) microspheres. ^b Specific surface area. ^c Pore volume. ^d Mean pore size. ^e The concentration of Ag in the poly (EGDMA) microspheres was detected by AAS measurements. The figure in the bracket corresponds to the concentration of Ag deposited onto the non-functionalized porous poly (EGDMA) microspheres.

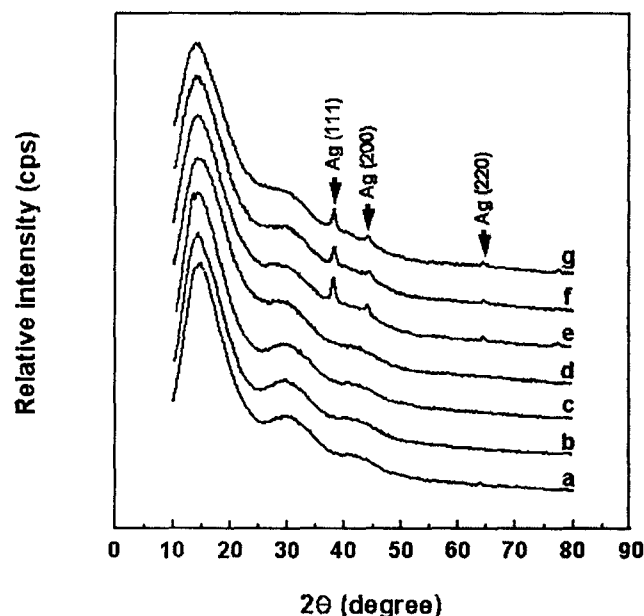


Figure 2. SEM and EDX photographs of Ag/poly(EGDMA) microspheres. Images, (a) and (b) are SEM photographs for outer and inner surfaces of Ag/poly(EGDMA/OH)-40. (c) and (d) are EDX photographs for outer and inner surfaces of the same sample, respectively.

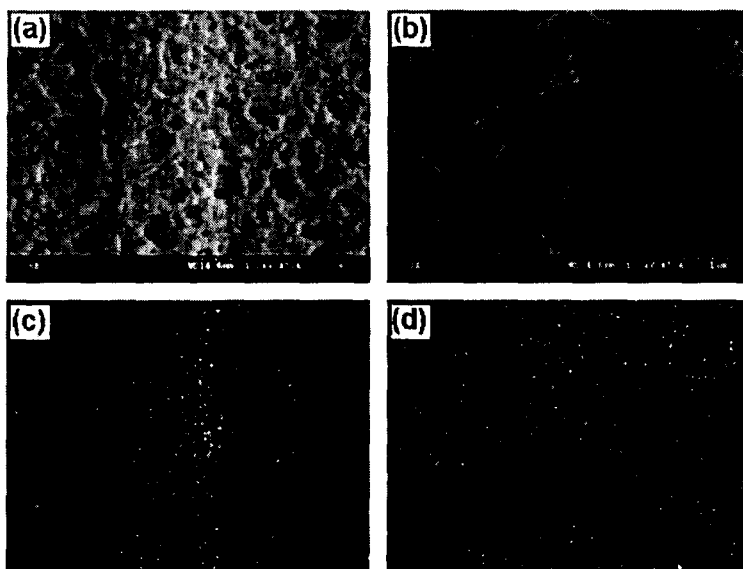


Figure 3. XRD patterns of Ag/poly(EGDMA) microspheres: (a) poly(EGDMA)-0, (b) Ag/poly(EGDMA)-0, (c) Ag/poly(EGDMA/OH)-0, (d) Ag/poly(EGDMA)-20, (e) Ag/poly(EGDMA/OH)-20, (f) Ag/poly(EGDMA)-40, (g) Ag/poly(EGDMA/OH)-40. In the deposition of Ag, the concentration of AgNO₃ was fixed with 3wt.% against total amount of poly(EGDMA) microspheres.

Phase characteristics of Ag/poly(EGDMA) microspheres

Continuously, we deposited colloidal Ag particles onto a series of poly(EGDMA) microspheres synthesized. After the deposition of colloidal Ag particles onto the poly(EGDMA) microspheres, the phase was characterized by XRD and shown in Figure 2. In the absence of Ag, only a typical XRD pattern for poly(EGDMA) could be observed. However, in the case of successful incorporation of Ag into poly(EGDMA) microspheres, three new peaks were detected in addition to the poly(EGDMA) XRD pattern, which correspond precisely to the face center cubic (fcc) Ag phase (111, 200, 220). The value of the Ag lattice constant has been estimated to be $a=4.081\text{\AA}$, a value which is consistent with $a=4.086\text{\AA}$ reported by the JCPDS file n^o 4-0783. In those XRD patterns, it is evident that the phase of Ag was characterized by the surface structure of the supporting microspheres. The fcc Ag phase formed feasibly depending mainly on the surface area of the microsphere. When the surface area was large enough, a larger amount of Ag was detected in the measurement of AAS (refer to Table 2). This result verifies that a larger surface area of the supporting polymer microspheres provided the reducing Ag ions with a sufficient deposition site. Additionally, the surface functionalization of poly(EGDMA) microspheres showed an influence on determining the degree of deposition of colloidal Ag particles. In our observation, the surface having hydroxyl functional groups had a tendency toward enhancing the degree of deposition of colloidal Ag particles. This reveals that the pendent hydroxyl groups on the surface made a contribution to improve an affinity for Ag particles. To ensure the distribution of colloidal Ag particles in the poly(EGDMA) microspheres, Ag/poly(EGDMA/OH-40), the Ag colloid phase was visualized

by SEM and EDX measurements and shown in Figure 3. In the spot EDX images detected at the same region with SEM, it can be visualized directly that colloidal Ag particles were deposited uniformly along with the outer and inner surfaces of the microspheres. The result obtained in this study demonstrates that to achieve a sufficient deposition of colloidal Ag particles, the supporting polymer microspheres should be designed considering the surface characteristics: especially, the surface area and the surface functionality.

Anti-microbial efficacy of Ag/poly(EGDMA) microspheres

It has been known well that Ag has many biological functions [11]. In order to evaluate a biological function in the form of Ag/polymer colloidal system, the anti-bacterial efficacy of Ag/poly(EGDMA) microspheres, Ag/poly(EGDMA/OH-40) was tested in a standard O/W emulsion formulation and shown in Figure 4. In this study, the preservation efficacy was evaluated by counting the number of bacteria in the sample with the incubation time at 32°C. In the absence of Ag component, anti-bacterial property could not be observed any more. The number of bacteria remained constant. However, by adding the Ag/poly(EGDMA) microspheres into the test formulations, the number of bacteria was decreased dramatically. Moreover, as the concentration of Ag/poly(EGDMA) microspheres increased, the number of bacteria was decreased much more sharply. Within a week, most of the initially inoculated bacteria were sterilized completely. This indicates that the Ag/poly(EGDMA) microspheres had a powerful anti-bacterial activity.

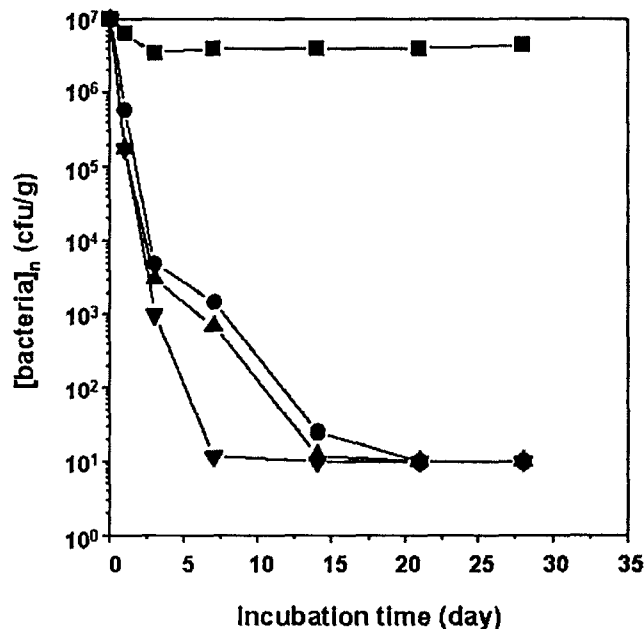


Figure 4. Preservation efficacy of Ag/poly(EGDMA) microspheres with varying their concentration in an O/W emulsion formulation: 0 wt.% (-■-, Ag 0ppm), 0.05wt.% (-●-, Ag 1.35ppm), 0.1 wt.% (-▲-, 2.7ppm), 0.2 wt.% (-▼-, 5.4ppm). In this experiment, Ag/poly(EGDMA/OH)-40 was used.

In order to confirm the maintenance of initial activity, the same samples tested were stored for 40 days at room temperature, and then, the preservation efficacy was evaluated again and shown in Figure 5. The number of bacteria was decreased with a similar fashion to that in Figure 4. Relative to these results, it was presumed that even though the colloidal Ag particles were anchored inner and outer surfaces of the microspheres, the ionization process of Ag was considerably facilitated from the surface and through the pore channel simultaneously.

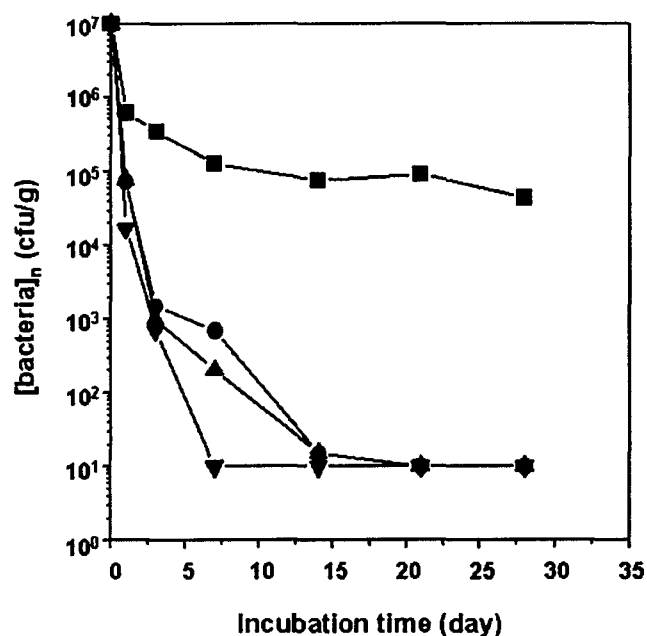


Figure 5. Preservation efficacy of Ag/poly(EGDMA) microspheres with varying their concentration in an O/W emulsion formulation after storage for 40 days at room temperature: 0 wt.% (-■-, Ag 0ppm), 0.05wt.% (-●-, Ag 1.35ppm), 0.1 wt.% (-▲-, 2.7ppm), 0.2 wt.% (-▼-, 5.4ppm). In this experiment, Ag/poly(EGDMA/OH)-40 was used.

Long-term stability of Ag/poly(EGDMA) microspheres

When Ag-containing formulations are stored for a long time, their color turns yellow or dark yellow. This phenomenon causes a serious problem in final applications. Therefore, in the real application of Ag in the formulations, no change in color is a preliminary requirement. The color change of Ag-containing O/W emulsions was observed by OM and UV-vis spectra measurements and shown in Figure 6 after 6-month storage at 40°C. The O/W emulsion containing conventional colloidal Ag nanoparticles changed eventually from white to dark yellow after long-term storage. In the UV-vis spectra measurements, even though typical absorbance could be detected at around 410nm, the Ag particles in the color-changed formulation had a broader absorption band to the visible light region. It is assumed that a secondary reduction reaction of the ionized Ag ions made new Ag particles in the formulation with aid of potential reducing agents, such as surfactants, chelating agents, and alcohols. On the contrary, in the case of using Ag/poly(EGDMA) microspheres, there

was no change in color. In the UV-vis spectra, it was found that the typical absorbance at 410nm was disappeared, irrelative to the storage condition. This means that the Ag nanoparticles anchored on the surface of porous poly(EGDMA) microspheres was not influenced by the applied UV and/or visible lights, because the polymer protect the light in advance. Moreover, if new Ag particles were generated by the secondary reduction reaction, they would be adsorbed much more favorably onto the hydroxy functional surface of poly (EGDMA) microspheres due to the strong interaction.

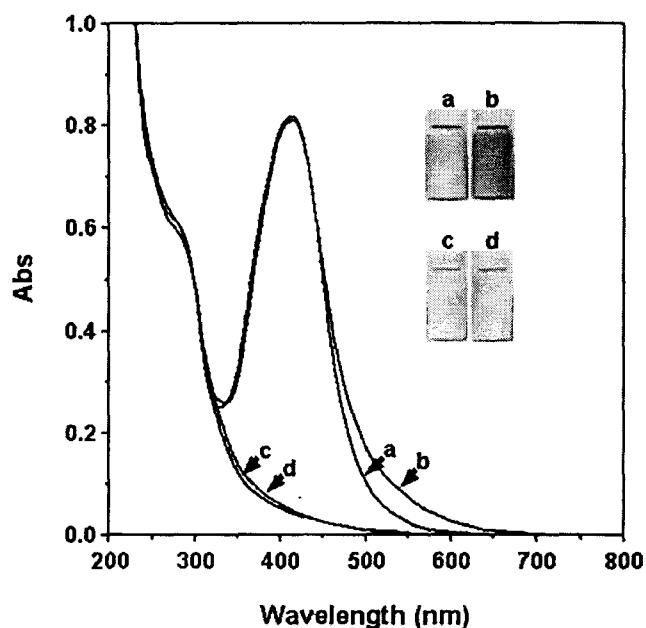


Figure 6. UV-vis spectra for the O/W emulsions containing colloidal Ag nanoparticles (a : right after preparation, b : after 6-month storage at 40°C) and Ag/poly(EGDMA) microspheres (c : right after preparation, b : after 6-month storage at 40°C), respectively. All the formulations contain 10 ppm of Ag.

Conclusions

In conclusion, this study describes that in situ deposition of colloidal Ag particles onto the functionalized porous polymer microspheres is a useful method for the composition of metal nanoparticles with colloidal polymer matrix. Structurally controlled-surface of the microspheres played an important role in anchoring effectively colloidal Ag particles and displaying their own biological function. Moreover, by controlling the pore structure of the microspheres, the reduction behavior of Ag ions could be confined within the surface, preventing successfully the browning phenomenon of conventional colloidal Ag particles. This technique presents a new avenue for advanced biological materials, in particular, those for anti-microbial applications in cosmetic industry.

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