

Synthesis of Monodisperse Nickel-Coated Polymer Particles by Electroless Plating Method Utilizing Functional Polymeric Ligands

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ABSTRACT: In the electroless plating process, to omit a sensitizing process with SnCl₂, we utilized amino-functional groups on polymer particles. At first, highly monodisperse functional polymer particles could be prepared by a two-step seeded polymerization of styrene, divinylbenzene, and glycidyl methacrylate. Then, surface epoxy-functional groups were converted to amino-functional groups by treating the particles with a diamine. By using these surface amino functionalities, we tried to prepare uniformly metal-coated monodisperse polymer particles by electroless plating method. The constituents of an electroless nickel solution bath are nickel salt, a reducing agent, suitable complexing agents, and stabilizers. And the metal thickness was simply controlled by changing the loading amount of substrate polymer particles. Morphological observation of nickel-

plated polymer particles was conducted by using optical microscopy, scanning electron microscopy, and transmission electron microscopy. The structural composition of plated nickel was also investigated. Most of all, the function and the efficiency of the amino-functional group of polymer particles as a polymeric ligand for metal binding was elucidated. From all observations, it was evident that in the electroless metal plating process without any sensitization step, the deposition of metal clusters on substrate particles is largely dependent upon the particle surface functionality. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3801–3808, 2006

Key words: electroless plating; monodisperse polymer particles; seeded polymerization; surface functionality; nickel coating

INTRODUCTION

Metal-coated polymer particles in the size range of 1–10 μm or larger have received great attention in many industrial fields such as medical science,¹ catalytic applications,² and some electronic packing technologies.^{3,4} For the above applications, highly monodisperse, micron-sized polymer particles are quite required owing to the same surface activity and the optimization of material efficiency. Dispersion polymerization has been reported to be one of the useful methods to obtain monodisperse, micron-sized polymer particles. In addition, to provide specific characteristics, such as the crosslinking, the functionality, the porous structure, the phase separation, etc., into polymer particles in a size range of 10 μm or above, several methods referred to as seeded polymerization have been often employed.^{5–8} In seeded polymerization,

because monomers are incorporated stepwise into the seed polymer particles and polymerize consecutively, the monodispersity of final particles can easily be attained by utilizing monodisperse seed particles. So, depending on the nature of the seed particles and the swelling monomers, a variety of monodisperse polymer particles can be produced by the seeded polymerization method.

The metallization of polymers has usually been carried out by vacuum deposition, sputtering, or electroless plating.^{9,10} Among various techniques, the electroless plating technique has widely been employed as a method of forming a metallic thin film on the surface of electrically nonconductive three-dimensional fine substrates, typically polymer particles. Principal reasons for the widespread commercial and industrial use of the electroless plating technique are to be found in unique properties of electroless metal deposits; chemical and physical properties of an electroless metal coating depend on its composition, which, in turn, depends on the formulation and operating conditions of the electroless plating bath. Except for electroless deposition, the fundamentals of the other metal-coating techniques are based on physical adsorption process, and generally used to coat metal on the thin layer film.

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In the electroless plating, a metal ion to be plated is reduced with a reducing agent in a plating solution and deposited on a substrate under metallic state. To start and accelerate the reducing reaction on the surface of a polymeric substrate, the polymeric surface must be first sensitized by SnCl_2 or CuCl_2 as initial cleaning and etching of dielectric substrate by physical or chemical means to improve the adherence of metallic coating.^{11,12} The sensitized surface was then activated by catalytic metal ion such as PdCl_2 and finally a noble metal (Ni, Au, Co, Cu, and Ag) is deposited on polymer surface by electroless plating. A single-step process of noble metal catalysts is also known, such as a solution of SnCl_2 and PdCl_2 .^{13–15} More recently, the sensitizing process with SnCl_2 solution could be omitted by introducing surface functional groups onto polymers and details of the electroless plating of functional polymer particles were given by Warshawsky and Upson.¹⁶ The functional group of polymers serves as a catalytic site of activation through binding of noble metal ions by coordinate or ionic bonds, followed by reduction to zero-valent noble metal complexes. Effective polymeric ligands reported are strong nucleophiles such as amino, carboxyl, and quaternary amino groups on the polymer surface.

In our previous study,¹⁷ we investigated the effectiveness of the surface thiol functionality of polymer microspheres in the electroless metal deposition. Micron-sized thiol group-containing polymer particles were prepared by a two-step seeded polymerization method and then zero-valent nickel was adsorbed on the polymer surface by an electroless deposition process. It was confirmed that polymer/Ni core/shell composite particles could be achieved by chemical metal deposition without a surface sensitization process, and it was possible by introducing the thiol group onto the particle surface as a site for coordinating with nickel ions. However, some undesirable crack in the Ni shell layer was observed, which may be due to inefficient binding affinity of the thiol group, unstable chemisorption of reduced colloidal Ni particles, or rapid reduction process. In this study, to improve the chemical adsorption of catalytic noble metal ion on the polymer surface, amino functionality was introduced onto monodisperse polymer microspheres, which were also produced by the seeded polymerization method. The selective activation of amino functional group on polymer particles leading to close control over the catalytic sites and, consequently, over the metal deposition process was investigated in view of the morphological and structural characterization of nickel deposits.

EXPERIMENTAL

Materials

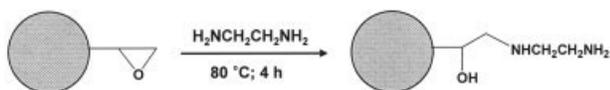
Styrene (St, Junsei Chemicals, Japan), glycidyl methacrylate (GMA, Junsei), divinylbenzene isomer (DVB,

~80% assay, Fluka, USA), 1-chlorododecane (CD, Tokyo Chemical Industries, Japan), and ethylene diamine (Junsei) were all reagent grades. Benzoyl peroxide (BPO, Junsei) was recrystallized from methanol before use. Poly(vinyl alcohol) (PVA, $M_w = 8.8 \times 10^4 - 9.2 \times 10^4 \text{ g mol}^{-1}$, 87–89% hydrolyzed, Kuraray, Japan) and sodium lauryl sulfate (SLS, Wako Pure Chemical Industries, Japan) were used as received. In the electroless plating process, palladium chloride (PdCl_2 , Samchun Chemical, Korea), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Aldrich, USA), sodium hypophosphite hydrate ($\text{NaH}_2\text{PO}_2 \cdot x\text{H}_2\text{O}$, Aldrich), sodium citrate dihydrate (Aldrich), and ammonium chloride (Samchun) were used as received.

Preparation of amino-functional monodisperse polymer microspheres

Highly monodisperse functional polymer particles could be prepared by a two-step seeded polymerization, following our previous experimental procedures.^{17–19} Uniform polystyrene (PS) particles were prepared by dispersion polymerization¹⁹ and used as seed particles. The swelling and polymerization procedure of the seeded polymerization was carried out in a four-neck glass reactor equipped with a mechanical stirrer, a refluxing condenser, thermocouples, and a nitrogen gas inlet system. First, PS seed particles (0.5 g) redispersed in a 0.25% SLS aqueous solution were swollen with CD (0.5 g) emulsified by ultrasonic homogenization in a 0.25% SLS aqueous solution. After the complete swelling of CD droplets, the monomer mixture of St (3 g), DVB (2 g), GMA (5 g), and BPO initiator (0.1 g) was emulsified by the same emulsification method and poured into the reactor. The swelling was continued at 30°C for another 12 h. The monomer-swollen particles were then stabilized with PVA aqueous solution and the PVA concentration was fixed at 1 wt % of the total weight (250 g). After deaeration with a nitrogen gas, the polymerization was carried out at 80°C for 12 h. The particles produced were collected by centrifugation and repeatedly washed with water and ethanol, followed by drying under a vacuum at ambient temperature.

The surface epoxy group of the product poly(St-*co*-DVB-*co*-GMA) particles was changed into an amino functional group by reacting the particles with ethylene diamine at 80°C for 5 h. After the reaction, particles were recovered by centrifugation and repeatedly washed by centrifugation/redispersion cycles in water and ethanol, followed by drying under vacuum at ambient temperature. A reaction diagram of the surface amination is illustrated in Scheme 1. To determine the surface amine group concentration, a HCl titration method was applied.²⁰ Aminated particles were first dispersed in *m*-cresol and methanol was added and then the dispersion was titrated with an ethanolic HCl



Scheme 1 A schematic reaction diagram of the surface amination.

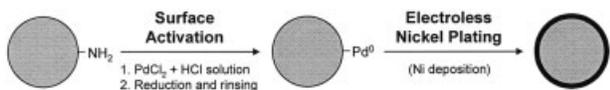
solution until the potentiometric equilibrium was reached. The potentiometric equilibrium was performed with tetrabutyl ammonium hydroxide. The titration was carried out at least twice.

Metal coating on polymer microspheres by electroless plating

Under the absence of sensitizing process with SnCl_2 solution, nickel-coated polymer particles were prepared by electroless nickel plating. First, amino-functional polymer particles were activated in an aqueous solution containing PdCl_2 (0.1 wt %) and HCl (1 wt %) for 10 min, and then rinsed with distilled deionized water to ensure complete removal of PdCl_2 ion, and then the coordinated Pd^+ complex was reduced to the Pd^0 complex by a 0.1 wt % sodium hypophosphite solution in water, at room temperature for 10 min. The dispersion of particles treated with Pd salt was pale brown. As the reduction of Pd ions proceeds, the color of the particle dispersion turned gray rapidly. Next, the activated polymer particles were dispersed in an electroless plating bath, composed of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 g/L), sodium citrate dihydrate (73.5 g/L), and ammonium chloride (40.1 g/L). The bath was heated to 80°C and the reducing agent sodium hypophosphite in an aqueous solution was introduced. The reaction was continued at this temperature for 1 h. Scheme 2 represents a simplified schematic diagram of overall electroless nickel plating process. After the electroless plating, the composite particles were separated by filtration, washed with water and ethanol, and dried in vacuo at 50°C for 24 h.

Characterization

The amino functional group introduced on the polymer surface was confirmed by Fourier transform infrared (FTIR) spectroscopy (Magna IR-550, Nicolet). Scanning electron microscopy (SEM), and energy-dispersive X-ray analysis (EDAX) measurements were performed using a JSM-6330F model from Jeol



Scheme 2 A schematic diagram of overall electroless nickel plating.

equipped with a Jeol EDAX probe. Typical electron energy was about 15 KeV and the acquisition time for EDAX measurements was about 150 s. The core/shell structure of metal-coated polymer particles was observed by transmission electron microscopy (TEM; JEM-2000, Jeol). For TEM observation, polymer/metal composite particles were dipped in epoxy matrix, cured at 60°C for 24 h, and then microtomed with a diamond knife. The ultrathin cross sections were put on a copper grid and observed by TEM. The structural state of coated metal layers was identified by the measurement of X-ray diffraction (XRD) patterns at a scanning rate of 5°min^{-1} , using a Rigaku D/Max-2200 (Copper radiation, 40 kV, 100 mA, a nickel filter) in the range of $2\theta = 10\text{--}80^\circ$. The content of metal plated was characterized by thermo gravimetric analysis (TGA; SDT2960, TA Instrument), operating in the temperature range of $30\text{--}600^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

RESULTS AND DISCUSSION

In the case without the sensitization process with a SnCl_2 solution, activation of selected functional groups is considered to be very important for the uniform metal plating of polymer particles. In addition, effective functional ligands are preferentially required for the formation of a well-controlled and evenly distributed catalytic layer on substrate polymer particles. Functional ligand groups that are conceived to be appropriate include neutral or cationic ligands, such as amino, imino, hydroxy, carboxylic acid, sulfonic acid, ammonium, oxonium, and sulfonium

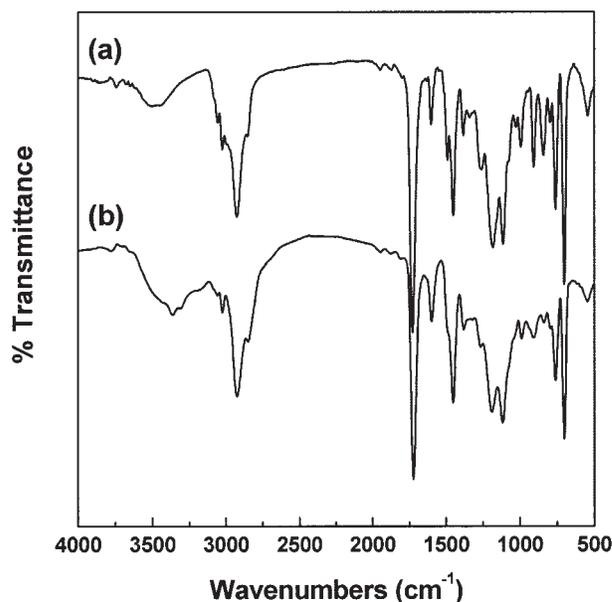


Figure 1 FTIR spectra of polymer particles before (a) and after (b) the amination process.

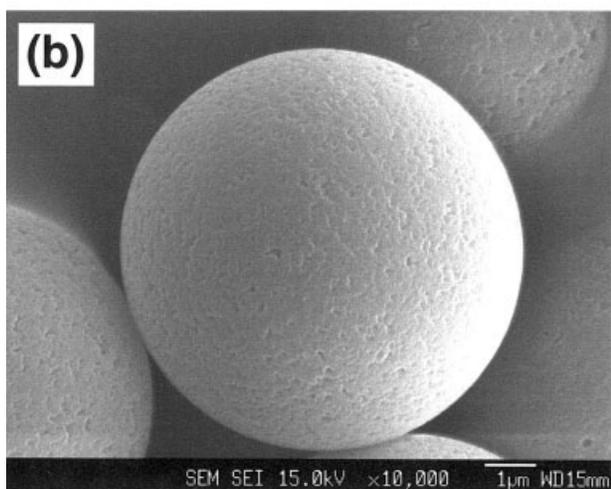
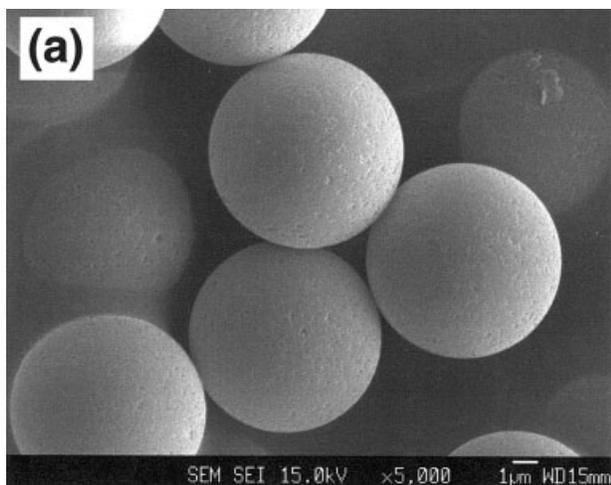


Figure 2 SEM photograph of substrate poly(St-co-DVB-co-GMA) particles (a) and their magnified image (b).

groups. Above all, nitrogen-containing functional groups are the preferred and wide-spread metal binders, forming stable complexes with zero-valent palladium.

In this study, we tried to introduce amino-functional groups onto polymer particles by treating pre-formed epoxy group-containing polymer particles. That is, the epoxy group of the GMA unit on the poly(St-co-DVB-co-GMA) particle was transformed to amino group by the reaction between epoxy group and ethylene diamine. Figure 1 shows FTIR spectra for polymer particles before and after the amination process. From the characteristic bands at 995 and 908 cm^{-1} of the FTIR spectrum [Fig. 1(a)], the presence of glycidyl ether groups in untreated polymer particles was confirmed. Though the glycidyl ether group in GMA may be opened by the crosslinking side reaction or the hydrolysis reaction during the polymerization process, it was previously revealed from an FTIR analysis that about 55–60% of glycidyl ether groups sur-

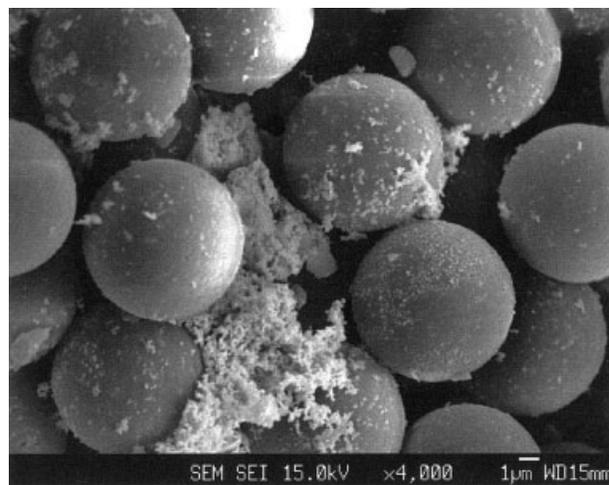


Figure 3 SEM photograph of polymer/Ni composite particles using untreated poly(St-co-DVB-co-GMA) particles.

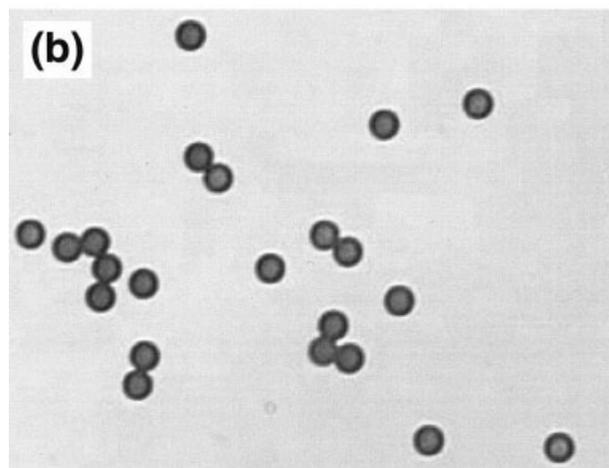
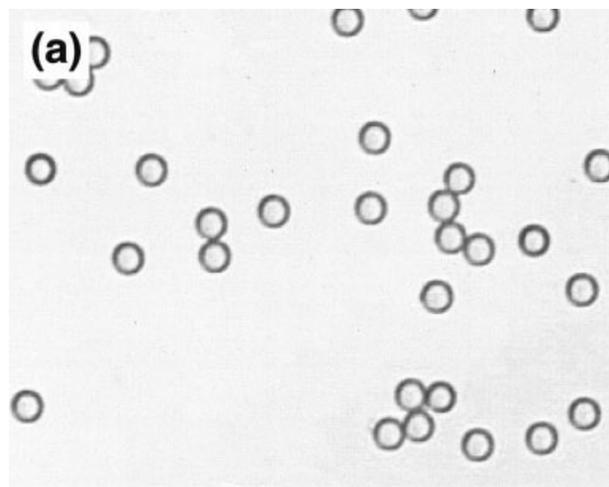


Figure 4 OM images of amino-functional polymer particles (a) and the corresponding polymer/Ni composite particles (b).

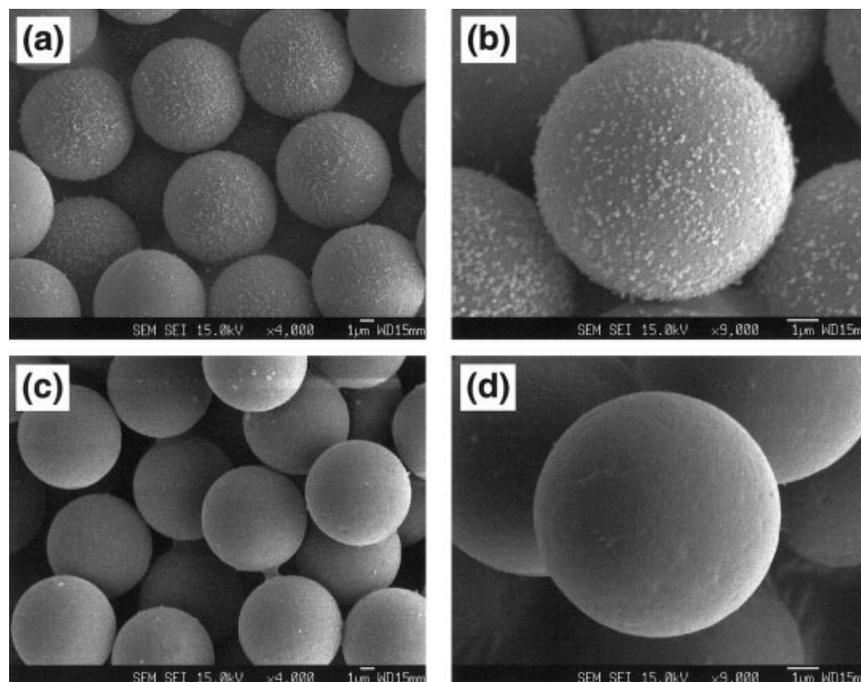


Figure 5 SEM photographs of Ni-coated composite particles using aminated polymer particles with initial GMA concentrations of 20% (a, b) and 50% (c, d).

vived the seeded polymerization.¹⁹ A broad band from about 3600 to 3200 cm^{-1} is attributed to the stretching vibration of —OH , which was formed by the ring-opening side reaction. The remaining glycidyl ether group on the particle surface could transform to amino functional groups. Particles after the amination process show distinct characteristic bands of stretching vibration of primary amines at 3363 and 3315 cm^{-1} [Fig. 1(b)]. In practice, the amine concentration obtained from the titration method was about 0.6 mmol g^{-1} . It is worth noting that the amine groups were successfully introduced onto the particle surface and the amount is expected to be sufficient for further chemical reactions.

Morphological properties of substrate polymer microspheres and their metallized particles were investigated by SEM and an optical microscope (OM). Figure 2 shows SEM photographs of substrate polymer particles. As clearly shown in the Figure 2(a), all the polymer particles produced were monodisperse in the size distribution and spherical in shape. Unexpectedly, very fine pores on the particle surface were also obtained [Fig. 2(b)], which may result from the high crosslinking density of secondary polymeric phase. As the polymerization proceeds, microphase separation between the secondary polymeric phase of DVB-crosslinked copolymer and the PS seed phase can occur in the seeded polymerization.²¹

As stated previously, all the electroless nickel plating were conducted under a condition in which the surface sensitization process was omitted. At first, the

electroless nickel plating was carried out on the untreated polymer particle, poly(St-co-DVB-co-GMA), which has no amino functional groups. As shown in Figure 3, small Ni particles or Ni aggregates were closely attached to the surface of polymer particles. It seems that Ni colloidal particles were partially adsorbed onto the polymer particle because the particles have fine porous surface aiding the physical adsorption between Ni colloids and polymer particles. However, the adsorption was quite nonuniform and a continuous Ni overlayer was not developed on the polymeric particle surface. Although untreated polymer particles have epoxy and/or hydroxyl functional groups on the surface, it seems that these groups cannot provide catalytically active binding sites for noble metal ions in the sensitizing-free plating process.

After the amination process of epoxy-functional polymer particles, electroless plating was carried out using these aminated polymer particles. Figure 4 shows OM images of amino-functionalized polymer particles and the corresponding polymer/Ni composite particles. The monodispersity of copolymer particles was maintained after the amination and the plating process. After the electroless plating process, Ni-metallized polymer particles exhibited dark gray or black color [Fig. 4(b)]. As one can see, all the particles were darkly colored, indicating that a Ni shell layer around the particle was uniformly formed. In general, the light absorption and reflection properties of the metal-coated polymer particles are related to the thick-

ness of the metal layer; therefore the dark color of the polymer/Ni composite particles reveals that a sufficiently thick metal layer was generated on the particle surface.

Typical SEM photographs for Ni-coated composite microspheres utilizing different concentration of amino functionality are shown in Figure 5. The GMA concentration of initial polymer particles for samples of Figure 5(a,b) and 5(c,d) were 20 and 50%, respectively. These substrate polymer particles were named PG20 and PG50, respectively, and the surface amine concentrations after the amination process were different from 0.2 mmol g^{-1} to 0.6 mmol g^{-1} . Figure 5(a) and (b) showed many islands of Ni particles adhered on the polymeric surface, not giving a continuous Ni layer. But it did not show severe Ni aggregates or the formation of free colloidal Ni particles like in Figure 3. On the other hand, the Ni-coated polymer particle using sufficient amino-functional polymeric ligands exhibited a smooth surface and a continuous Ni layer on the polymer particle [Fig. 5(c,d)]. From a magnified photograph of polymer/Ni composite particles [Fig. 5(d)], it was more evident that the surface of polymer particles was wholly covered with a uniform and smooth nickel layer. And there were no cracks in the Ni coating layer. From the results, it was confirmed that sufficient amino-functional groups could serve as a catalytically active site for uniform metal deposition. As stated before, in our previous study,¹⁷ chloromethyl styrene of 30% against the total monomers was incorporate into the polymer particles by seeded polymerization; then the surface chloromethyl group was converted to thiol group. Though the particles bearing thiol functionality also provided thick and uniform coating of Ni layer, it showed relatively low adherence of metal layer to the polymer surface, giving fine cracks in metal layer. Taking into consideration that about 40% of glycidyl ether groups are unexpectedly cleaved into hydroxyl groups during the polymerization and so valid glycidyl groups for amination is reduced, the concentration of surface functionality of polymer particles (PG50) with initial GMA content of 50% are thought to have almost the same as particles of the previous work. From this point of view, the amino functionality is believed to be more effective for the formation of a stable and uniform Ni layer than the thiol functionality considered in our previous study.¹⁷

Figure 6 shows typical TEM photographs of the cross section of polymer/Ni composites using PG20 and PG50 particles. As like in SEM results, TEM result also showed that not a continuous layer but colloidal domains of Ni were formed colloidal domain of Ni on the surface of PG20 polymer particles having small amine groups [Fig. 6(a)]. While with PG50 polymer particles, it was found that a continuous and uniform Ni layer was formed around the polymer microsphere

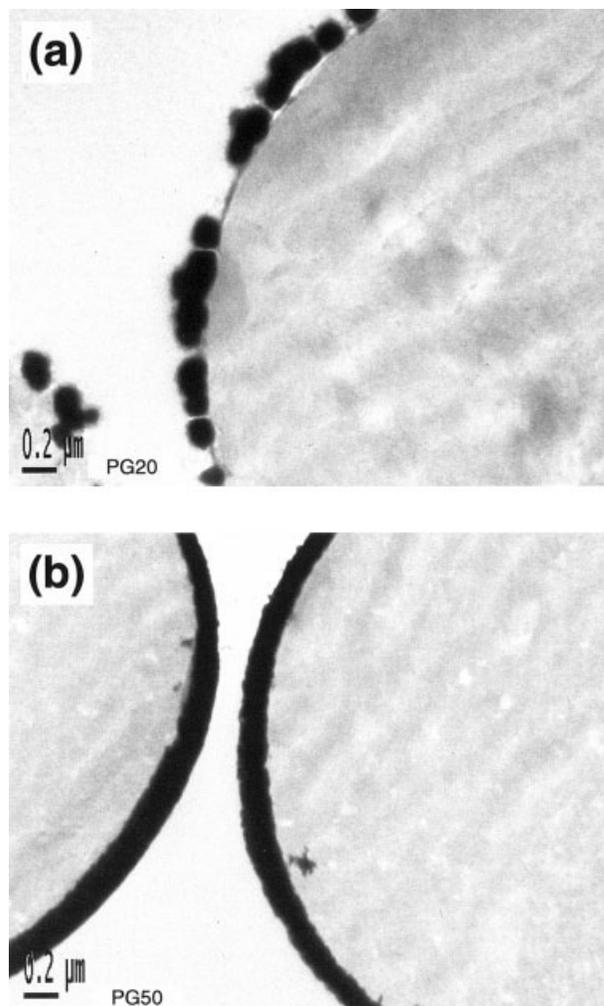


Figure 6 TEM photographs of the cross section of Ni-coated composite particles using aminated polymer particles with initial GMA concentrations of 20% (a) and 50% (b).

[Fig. 6(b)]. In addition, the thickness of coated Ni layer was controlled by varying the workload of polymer particles in the plating process. Hereafter, monodisperse polymer microspheres having sufficient amino-functional groups were used to prepare polymer/metal composite particles by the electroless plating. The thickness of coated Ni layer was calculated from an image analysis of magnified TEM photographs. It was found that the thickness of the metal layer depends directly on the workload of polymer particles during the chemical metal deposition process, and the value attained ranged from 36.4 to 175.1 nm. Characteristics of Ni-coated polymer composite particles are listed in Table I.

The metallized polymer particles were characterized by EDAX and XRD for the evaluation of their structure and composition. The EDAX patterns for the metallized polymer particles are shown in Figure 7. The EDAX patterns show the presence of Ni and P in the composite particle. The average atomic ratio of

TABLE I
Characteristics of Nickel-Coated Polymer Microspheres
Prepared by Electroless Plating Method

Sample name	Substrate workload ^a (g/L)	Ni layer thickness (nm)
P050-Ni1	10.0	36.4
PG50-Ni2	5.0	74.1
P050-Ni3	2.5	175.1

^a The workload amount of substrate polymer particles during the electroless nickel plating process at a constant nickel salt concentration.

Ni/P was calculated to be 90.6/9.4 by the EDAX analysis. This result points out that the surface of the composite particle is rich in metal covering the surface of polymer microspheres. XRD profiles of the amino-functionalized polymer particles and their Ni composite particles are shown in Figure 8. The wide reflection at $2\theta = 19^\circ$ is assigned to amorphous amino-functionalized polymer particles and a strong reflection at $2\theta = 44.1^\circ$ observed in Figure 7(b) is attributed to the (111) plane of zero-valent Ni. This indicates that the zero-valent Ni was deposited on the substrate polymer particles by coordinate or ionic bond.

For the measurement of Ni-P content on the amino-functional polymer particles, the thermogravimetric analysis (TGA) was used. TGA curves for the amino-functional polymer particles and their Ni composite particles are shown in Figure 9. On behalf of all Ni composite particles, one composite sample (PG50-Ni2 in Table I) was used for the TGA experiment. The weight loss up to 600°C was calculated to be 92.9 wt % and 74.6 wt % for the amino-functionalized polymer particle and their Ni composite particles, respectively. The weight loss in this temperature range is mostly attributed to the degradation of polymeric chains. Therefore, the difference between the residue contents is attributed to the chemically deposited Ni on the polymer particles by the electroless plating.

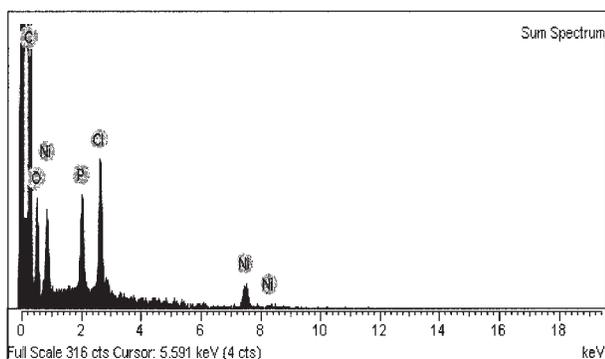


Figure 7 EDAX patterns of polymer/Ni composite particles.

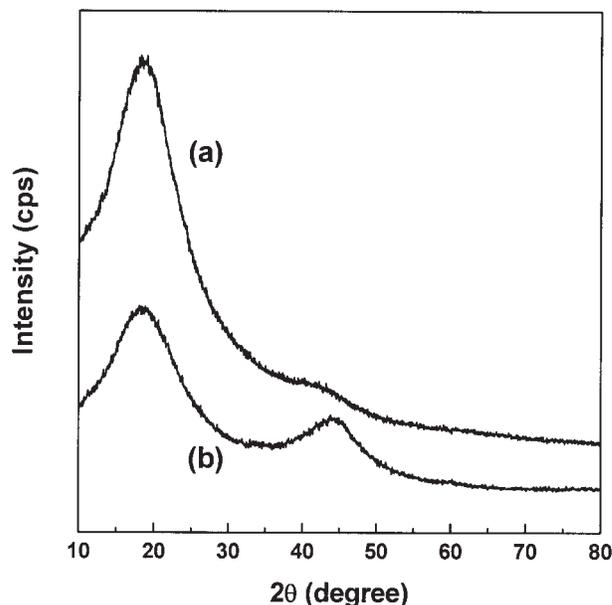


Figure 8 XRD patterns for amino-functional polymer particles (a) and the corresponding Ni-coated particles (b).

CONCLUSIONS

Monodisperse amino-functional polymer particles in micron-size range were successfully prepared by the two-step seeded polymerization and postamination treatment. The Ni-coated polymer particles could be obtained by an electroless plating using amino-functional groups of the polymeric particle surface. It was found that the surface amino functionality of the polymer particle had significant effect on surface catalyzing and adhering of reduced metals onto the substrate surface. From the direct observation of TEM photographs, it was found

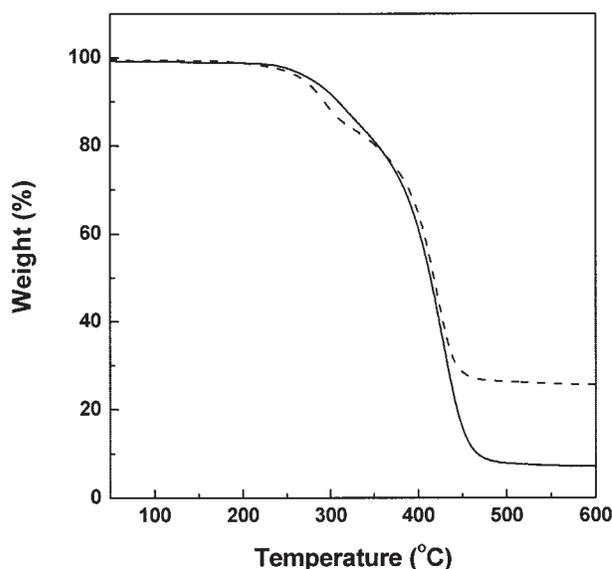


Figure 9 TGA thermograms of the amino-functional polymer particles (—) and their Ni-coated particles (---).

that Ni-coated polymer particles have Ni layer thickness of up to ~175 nm depending on the particle workload to be plated. Also, TEM images provided the direct confirmation of the continuous and uniform Ni coating layer. EDAX and XRD analyses showed distinct characteristic bands of the deposited Ni layer. Moreover, from all of the results, it can be concluded that the amino-functional particles are more efficient to get a stable and smooth metal coating than the thiol-functional particles for the electroless plating in the absence of sensitizing etching process. Therefore, these functional polymer particles have great advantage that the polymeric functional groups can serve as effective ligands of metal binding, eliminating the sensitization step of an electroless metal plating procedure.

References

1. Gupta, P. K.; Hung, T. C.; Lam, F. C.; Perrier, D. G. *Int J Pharm* 1988, 43, 167.
2. Tibbit, J. M.; Gates, B. C.; Katzer, J. R. *J Catal* 1975, 38, 505.
3. Isao, T.; Yutaka, Y.; Atsuo, N.; Yasushi, G. U.S. Pat. 5,001,542 (1991).
4. Oyamada, M.; Abe, S. U.S. Pat. 6,770,369 (2004).
5. Wanderhoff, J. W.; El-Aasser, M. S.; Micale, F. J.; Sudol, E. D.; Tseng, C. M.; Silvanoaicz, A.; Kornfeld, D. M.; Vincent, F. A. *J Dispersion Sci Technol* 1984, 5, 231.
6. Ugelstad, J.; Kaggerud, K. H.; Hansen, F. K.; Berge, A. *Makromol Chem* 1979, 180, 737.
7. Ugelstad, J.; Mørk, P. C.; Kaggerud, K. H.; Ellingsen, T.; Berge, A. *Adv Colloid Interface Sci* 1980, 13, 101.
8. Okubo, M.; Shiozaki, M.; Tsujihiro, M.; Tsukuda, Y. *Colloid Polym Sci* 1991, 269, 222.
9. Duffy, J. I.; *Electroless and Other Nonelectrolytic Plating Techniques: Recent Developments*; Noyes: Park Ridge, NJ, 1980.
10. Mallory, G. O.; Hajdu, J. B. *Electroless Plating: Fundamentals and Applications*; American Electroplaters and Surface Finishers Society: Orlando, FL, 1990.
11. Bergstrom, E. A.; Lidingo, S. U.S. Pat. 2,702,253 (1955).
12. Shirahata, R.; Suzuki, M.; Yamada, Y.; Kitamoto, T.; Dezawa, S. U.S. Pat. 4,089,993 (1978).
13. Zeblicky, R. J. U.S. Pat. 3,672,923 (1972).
14. Tsukahara, M. *J. Met Finish Soc Jpn* 1972, 23, 83.
15. de Minjer, C. H.; Boom, P. F. J. V. D. *J Electrochem Soc* 1973, 120, 1644.
16. Warshawsky, A.; Upton, D. A. *J Polym Sci Part A: Polym Chem* 1989, 27, 2963.
17. Park, J. G.; Kim, J. W.; Oh, S. G.; Suh, K. D. *J Appl Polym Sci* 2003, 87, 420.
18. Kim, J. W.; Suh, K. D. *Macromol Chem Phys* 2001, 202, 621.
19. Park, J. G.; Kim, J. W.; Suh, K. D. *Colloid Polym Sci* 2001, 279, 638.
20. Pittman, C. U., Jr.; He, G. R.; Wu, B.; Gardner, S. D. *Carbon* 1997, 35, 333.
21. Chen, C. M.; Vanderhoff, J. W.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1992, 30, 245.