Preparation of P(MMA/EGDMA/GMA)/Ni functional composite particles by dispersion polymerization and electroless plating

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Abstract-In this study, copolymer beads were prepared from glycidylmethacrylate (GMA) and methylmethacrylate (MMA) in the presence of a cross-linker (i.e., ethyleneglycol dimethacrylate,EGDMA) via dispension polymerization. Preparation of P(MMA/EGDMA/GMA)/Ni functional composite particles that the synthesis particles having various size from 0.5 to 5 μ m by dispersion polymerization which the particle size was controled with initiator concentration, and polymerization temperature. In this study,Poly(MMA/EGDMA /GMA)/Ni beads were synthesized by dispersion polymerization and electroless nickel. The core-shell structure of polymer--nickel composites and the structure of polymer spheres were characterized by TGA, FESEM,EPMA and FTIR. The results indicate that the nickel was coated on the surface of microspheres. The inner diameter of the microspheres with nickel shell was about 0.6~1.6 μ m. A possible formation mechanism of the core-shell structure of P(MMA/EGDMA /GMA)/Ni spheres was proposed.

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1. Introduction

Anisotropic conductive adhesive (film) provides both electrical and mechanical interconnections between electronic components and the supporting substrate. These anisotropic conductive films (ACFs) offer numerous advantages in surface mount assembly, including flexible and simple process at low temperature, fluxless bonding which eliminates the need for cleaning, lead-free formulations and low cost [1,2]. The anisotropic nature of these materials makes them excellent candidates for very fine pitch component such as flip chip. These flip chip applications on flexible substrates such as smart cards, disk drives and driver chips for LCDs have attracted much interests andwid espreaduse [3]. However, in flip chip technology, ACF dose not selfalign [4] that would allow misplaced chips to be pulled into correct position corresponding to substrate electrodes by surface tension forces of molten solder.

Composite particles that contain an inner core covered by a shell (core-shell particles) exhibit significant different properties from those of the core itself. The surface properties are governed by the characteristics of the shell coating. The surface engineering of particles is to produce core-shell particles, where the core consists of a solid coated by a number of methods. We have introduced the metallic nickel component into co-polymer cores using electroless plating to form composite particles with response to external electric fields.

Poly(methyl methacrylate)-(glycidyl methacrylate)-(ethyl dimethacylate), glycol poly(MMA-GMA-EGDMA) particles were prepared polymerization. bv dispersion Conventional, poly(GMA-MMA-EGDMA) beads were prepared via suspension polymerization. This work examines the feasibility of adopting a novel dispersion method [5-11], as seldom done polymerization previously. to polymerization the copolymer microsphere. The epoxy group containing poly(glycidyl methacrylate-co methylmethacrylate) beads were prepared by dispersion polymerization and the beads were cross-linked with ethyl glycol dimethacylate (EGDMA). The functional epoxy groups of the beads were converted into amino groups. The size and structure of the beads were characterized using SEM and FT-IR spectroscopy, respectively.

Recently, The epoxy groups of the beads were converted into amino groups has been used as a polymeric cross linking agent of latices with epoxy groups, to reduce the release of harmful components into the environment, and to enhance the properties of water and solvent resistance and the mechanical strength of the films formed from the latices.[12] However, highly hydrophilic polymers are not easily prepared by conventional polymerization. Dispersion polymerization might give monodisperse microspheres but the polymerization is apt to leave free stabilizers in the medium, which would be a harmful contaminant in their applications.[13,14]

In this paper, the Ni-coated Poly(MMA/EGDMA /GMA) microspheres were fabricated by electroless plating. The surface activating treatment and electroless nickel plating process were optimized in order to obtain the uniform and continuous coatings. And the electrical properties of Ni-coated Poly(MMA/EGDMA /GMA) microspheres were also investigated in order to develop the novel conductive microparticles.

2. Experimental Setup

2.1. Materials

Methyl methacrylate (MMA, ACROS Chemicals). glycidyl methacrylate (GMA, ACROS Chemicals). ethyl glycol dimethacylate (EGDMA; Kishida Chemical Industries, Tokyo, Japan) were of commercial grade. They were each distilled under reduced pressure and stored in a refrigerator before use. 2,2_-Azobisisobutyronitrile (AIBN; ACROS Chemicals) was used as a hydrophobic initiator for the suspension polymerization and dispersion polymerization.

2.2. Polymerization for dispersion polymerization

Dispersion polymerization was carried out in a 250 mL round flask with a mechanical stirring at 200 rpm under nitrogen atmosphere at 70 °C. Preweighed ethanol and aqueous PVP solution were charged in the reactor and followed the addition of MMA, GMA and EGDMA. Then, the AIBN dissolved in ethanol was added and the initiated. polymerization was During the polymerization, aliquots of the reaction mixture were withdrawn from the reactor to examine the conversion upon reaction time and the characteristics of the particles. The withdrawn polymerization products were rinsed off with DDI water and ethanol, centrifuged repeatedly to remove the nonreacted materials and dried in vacuum oven at 60 °C for 2 days, then used for characterization. The detailed polymerization method and the optimum conditions for the preparation of monodisperse polymer particles are described in the elsewhere.

2.3. Nickel nanoparticles coating on PMMA-GMA-EGDMA polymer spheres

Nickel was coated onto PMMA-GMA-EGDMA copolymer beads by electroless plating. The known amount of parent PMMA-GMA-EGDMA particles were first sensitized using an acid SnCl₂ solution (0.1M SnCl₂/0.2M HCl) ultrasonically for 40 min. Then the mixture was washed with deionized water.

This step resulted in creating nanoscopic metallic Pd particles as catalytic sites on the PMMA-GMA-EGDMA particles surfaces. The Pd-modified particles were rinsed again using de-ionized water and introduced into electroles splating solution bath. The Pd catalytic sites created on the polymer sphere surfaces allow the second surface redox reaction to begin. These beads were rinsed repeatedly with de-ionized water. The beads were then immersed in an electroless Ni plating solution (ICP Nicoro GIB, Okuno Chemical Co. Ltd.,Japan) for 8 min at 80°C to produce an Ni layer under constant stirring. Finally, the product was separated by washed twice with de-ionized water.

2.4. Characterization

After the polymerization, the final monomer conversion was measured gravimetrically. The size and size distribution of MMA-GMA-EDGMA copolymers were observed by scanning electron microscopy (SEM, S-3500N; HITACHI, Japan) for the dispersion polymerization. Thermal gravimetric analysis (TGA) of PMMA-GMA-EGDMA was carried out on a TA-STDQ600 (TA Instruments, New Castle, DE). The thermograms were acquired between 25 and 500°C at a heating rate of 10°C/min. Nitrogen was used as the purge gas at a flow rate of 20 mL/min. Fourier transform infrared (FT-IR) spectra of the copolymer microsphere were recorded with a Nicolet (Madison, WI) 170SX FT-IR spectrometer in the attenuated total reflection mode, wavelength range 4000–650 cm⁻¹.

3. Results and Discussions

Dispersion polymerization is actually a precipitation polymerization in which the medium is miscible with the monomer but not the polymer. When the polymerization starts, free radicals formed by initiator decomposition grow in the continuous phase until their size reaches a critical chain length, at which point they precipitate by either a self or aggregative nucleation process[15], forming nuclei.

When sufficient mature particles are formed ehich can capture all the radicals and nuclei in the continuous phase, no more particles will be formed, and the particle formation stage is completed [16].

3.1. Microsphere thermal analysis

Fig.1. show the TGA thermographs of MMA-GMA-EGDMA copolymer microsphere. The TGA curves of MMA-GMA-EDGMA copolymer microsphere revealed there main weight loss regions. The first region at $80-150^{\circ}$ C was due to the removal of water; the second transition region at $200-400^{\circ}$ C was due to degradation of the polymer films; and the peak of the third stage, at 435° C, was due to cleavage

of the polymeric backbone. The temperature of hot loss weight analysis is 234°C. We find hot loss weight analysis result, PMMA-GMA-EDGMA copolymer micro sphere than one PMMA polymerization micro sphere of hot loss weight analysis. The reason has adding micro EDGMA that the structure inner take shape cross linking. The temperature increases of hot loss weight analysis.

3.2. Temperature

As illustrated in Fig.2 The copolymer prepared at temperatures of 70, 75 and $80^{\circ}C_{-}$ had narrow size distributions with the particle diameter increasing from 0.8 um at 70°C to 0.9 um at 75°C to 1um at 80°C



Fig.1. The PMMA-GMA-EDGMA copolymer microsphere of hot loss weight analysis.



Fig.2. Effect of temperature on copolymer particle size

3.3. Initiator concentration

Narrow particle size distributions were obtained for copolymer particles prepared with AIBN initiator concentrations ranging from 0.1 to 0.5 wt% at a constant concentration PVP of 5%. The particle size increased from 0.5 to 1um as initiator concentration was increased over this range.Fig.3. shows effect on initiator (AIBN) concentration on copolymer size.



Fig.3. Effect of initiator (AIBN wt%) on copolymer particle size

3.4. FT-IR analysis

The FT-IR spectrum of PMMA-GMA-EGDMA (shown in fig.4.) indicates the details of functional groups present in the synthesized polymer beads. A sharp intense peak at 1721 cm⁻¹ appeared due to the presence of ester carbonyl group stretching vibration. The broad peak ranging form 1260-1000cm⁻¹ can be explained owing to the C-O (ester bond) stretching vibration. The broad band from 950-650 cm⁻¹ is due to the bending of C-H. The broad peak ranging form 3100-2900 cm⁻¹ is due to the presence of stretching vibration. Have epoxy function groups in the structure of Glycidylmethacrylate. Because other function groups are too strong to cover the signal of epoxy function group in the polymer.



Fig.4. FT-IR spectra of MMA-GMA-EDGMA copolymer, MMA polymer

3.5. Microsphere morphology

The technique for electroless metal plating is based on the use of a chemical reducing agent that permits the reduction of the metal from solution on the surface of the substrate. For this process, the beads surfaces need not be electronically conducting, while the kinetics of electron transfer should be slow enough to avoid the reduction of the metal ions and nucleation in solution. The surface acts then as a catalyst to ensure that reduction only takes place on the surface, so that the metal remains attached. The scanning electron microscopy images of PMMA-GMA-EDGMA for dispersion polymerization polymer particles, shown in Fig.5. The presence of the loaded nickel nanoparticles on the PMMA-GMA-EDGMA polymer micro spheres can be confirmed initially by the scanning electron microscopy. While the SEM image of the nickel loaded particles, PMMA-GMA-EDGMA/ Ni particles, in Fig.6. clearly become opaquely black.



Fig.5. The SEM image of PMMA-GMA-EDGMA particles.



Fig.6. The SEM image of PMMA-GMA-EDGMA/Ni particles.

The primary importance of an Electron probe micro-analyzer (EPMA) is the ability to acquire precise, quantitative elemental analyses at very small "spot" sizes about 1~2 microns, EPMA analysis of

the PMMA-GMA-EGDMA/Ni particles, as shown in Fig.4, indicated that there were 89.77wt.% of nickel and 10.23 wt.% of phosphorous in the deposited nickel–phosphorous component. The phosphorous peak derived from the reducing agent, which is considered to affect the electric property of the Ni–P coating. Then,for comparison the Pd, Ni and P loading after step-by-step electroless plating was measured by ICP-MS. The loading was measured to be 0.35 wt%,35.65 wt% and 4.34 wt% after nickel plating, respectively. After the subsequent nickel deposition process, which corresponds to an average coating thicknesses of the Ni-P layers of 100~150 nm, shown in Fig.5.



Fig.7. Electron probe micro-analyzer analysis of PMMA-GMA-EGDMA/Ni particles.



Fig.8. Cross-section SEM images of the resulting PMMA-GM EGDMA/Ni particles 1 µm

4. Conclusions

In conclusion, the novel PMMA-GMA-EDGMA/Ni particles were prepared by nonelectroless plating technique. The resulting particles were of 0.8~1 um average diameter. This provided a new route to control and selective surface modification of colloidal particles.

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