Journal of Alloys and Compounds 473 (2009) 206–211

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Preparation of PS/Ag microspheres and its application in microwave absorbing coating

Wen Zhao[a], Qiuyu Zhang[b,*], Hepeng Zhang[b], Junping Zhang[b]

[a] Faculty of Life Science, Northwestern Polytechnical University, Xi'an, Shaanxi Province 710072, PR China
[b] Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, Shaanxi Province 710072, PR China

ARTICLE INFO

Article history:
Received 18 August 2007
Received in revised form 11 May 2008
Accepted 13 May 2008
Available online 25 June 2008

Keywords:
Coating materials
Chemical synthesis
Dielectric response
Microstructure
Scanning electron microscopy

ABSTRACT

PS/Ag microspheres were prepared by electroless silver plating on PS microspheres. The PS microspheres with the average size of 1.6 μm were obtained by dispersed polymerization. Pretreatment was performed to adsorb palladium catalytic active centers on the PS surface, prior to plating. Effect of reaction temperature and loadage was studied. The proper temperature for electroless silver plating is determined to be 20 °C, and the loadage should be restricted in the range of 2.80–3.50 g to achieve ideal silver coating. It is found that the density decreases from 2.82 g/cm^3 to 2.32 g/cm^3 while the loadage increases from 2.86 g to 4.29 g. SEM, EDS, and XRD proved the successful formation of silver coating on PS microspheres. A waterborne microwave absorbing coating, based on PS/Ag microspheres and waterborne acrylic resin as binder, was developed. The result shows that nearly 70% of the incident wave is absorbed by this microwave absorbing coating in the frequency range of 10–18 GHz.

1. Introduction

The microwave absorbing technology is a significant subject to fulfill civil and military purposes. Recently, the electromagnetic pollution was increased for the rapid development of electronic and telecommunication systems. Various microwave absorbing materials (RAM) was used to shield the electromagnetic interference (EMI) [1]. In the military area, the role of RAM is to reduce target detection by the radar, i.e., to reduce its signature for radar detection. Microwave absorbing coating is widely used in military field to cover the surface of targets, which consist of different types of equipment, land vehicles, aircraft and ships [2]. Generally, microwave absorbing coating is produced by combination of absorbing centers (fillers) with a polymeric matrix and some other assistant agent. In recent years, much attention has been focused on exploiting new types of light, broadband RAM.

Silver powder is a kind of excellent electronic conductive material which has wide uses in electric industry, civil, and military fields. But the high cost and density of silver powder become obstacles for the wide application. It can be expected that if silver were deposited on the surface of polystyrene microspheres, the composite powder would be obtained with silver as shell. The substitution of the composite powder for silver powder is a desirable option in many fields to solve the problems such as high cost and density. Electroless plating method has been widely used to fabricate various kinds of composite materials due to the advantages of its simplicity and high deposition rate. Nowadays, electroless silver plating has been adopted as an effective tool for nanofabrication and surface modification of various substrates, such as Cu powder [3], graphite [4], silica [5], Al_2O_3 [6], and so on. Low-density silver composite powder may be an excellent potential candidate for RAM by the mechanism of ohmic losses. To the knowledge of the authors, the application of PS/Ag microspheres in microwave absorbing coating has not been previously reported yet. For this reason, this research was carried out.

This paper deals with the preparation of PS/Ag microspheres by electroless plating method. In the present work, several parameters for plating were optimized in order to obtain an integrated and uniform silver coating. The properties of the PS/Ag microspheres such as chemical composition and crystal texture of the coating, and density were investigated. A waterborne microwave absorbing coating, based on PS/Ag microspheres and waterborne acrylic resin as binder, was developed. The absorbing performance of the microwave absorbing coating was evaluated at the frequency range of 2–18 GHz by using a reflection/transmission technique in the microwave anechoic chamber.

2. Experimental

2.1. Preparation of PS microspheres

Polystyrene (PS) microspheres were prepared by dispersion polymerization which comprises the 2,2-azobis (isobutyronitrile) (AIBN) catalyzed polymerization

* Corresponding author. Tel.: +86 29 88495304 801; fax: +86 29 88495304 801.
E-mail address: qyzhang1803@gmail.com (Q. Zhang).

0925-8388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.05.047

Table 1
Compositions of the electroless plating solution

Chemicals	Content
Silver salts solution	
$AgNO_3$	3.5 g
NaOH	2.5 g
H_2O	60 mL
$NH_3{\cdot}H_2O$ (28–30%)	10 mL
Reducing solution	
$C_6H_{12}O_6$	45 g
$C_4H_6O_6$	4 g
C_2H_5OH	100 mL
H_2O	1000 mL

of styrene in a water–ethanol solution in the presence of polyvinylpyrrolidone (PVP) as the stabilizer. Typically, 0.1 g AIBN and 0.7 g PVP were dissolved in 10 g St, 40 g water–ethanol solution, respectively. These two solutions were mixed into 250-mL three-necked glass vessel equipped with condenser, stirrer and thermometer. The vessel was immersed in a thermostated water bath. When the temperature increased to 75 °C, the reaction was carried out for 8 h. Pretreatment was carried out in colloidal palladium solution at 30–40 °C for a period of time, then the activated PS microspheres were separated from the activating solution, rinsed with distilled water and 10% (v/v) HCl, later, rinsed with distilled water.

2.2. Electroless silver plating on PS microspheres

The electroless plating solution is composed of silver salts solution and reducing solution, and their compositions are given in Table 1. Transparent silver salts solution was first prepared by dissolving $AgNO_3$ in water. Then brown precipitation was produced after addition of NaOH solution. Finally, aqueous ammonia was added until the silver salts solution became transparent again. Reducing solution was prepared by mixing the dissolved chemicals together. The silver salts solution and reducing solution were mixed with a ratio of 1/1 (v/v) just before used. Electroless silver plating on PS microspheres was performed by immersing the pretreated PS microspheres in 140 mL plating solution. Mechanical agitation was employed during plating process. After 40 min, the powders were filtered and rinsed with distilled water, then dried at 60 °C. Then, PS/Ag micospheres were obtained.

The compositions of the microwave absorbing paint are shown in Table 2. The PS/Ag microspheres were added and dispersed in acrylics acid resin R413B (obtained from Dow Chemical, USA), and the mixture's homogeneity was assured by mechanical mixing. Afterward, defoaming agent, dispersing agent, film-forming agent, water, and thickening agent were added, and then the mixture was stirred and grinded to achieve homogenous paint. According to the national standard of china GB1727-79, the paint was evenly brushed on the surface of high-intensity terylene cloth and tinplate. The size of terylene sample and tinplate sample is 30 cm × 30 cm and 5 cm × 12 cm, respectively. Then the painted terylene and tinplate were placed in a thermostated oven for 10 min, and the temperature was 120 °C.

2.3. Characterization

The surface morphologies of the PS/Ag microspheres were investigated by scanning electron microscopy (SEM) (Philips-FEI Quanta 200, Holand). The chemical compositions of the coating were analyzed by energy dispersion X-ray analysis (EDS) instrument (Oxford EDAX, UK). X-ray diffraction (XRD) with Cu Kα radiation was used to analyze the crystal texture of Ag-coating on a XRD instrument (Rigalcu D/max 3C, Japan). According to the national standard of china GB5161-85, the effective density of the PS/Ag microspheres was mensurated by liquid immersion method. Measurement of microwave property was carried out on the terylene sample, and measurement of mechanical properties were carried out on the tinplate samples. A network analyzer (Agilent E8363A Network Analyzers) was employed to test the microwave absorbing property of the coatings at the frequency range of 2–18 GHz by using a reflection/transmission technique. The microwave absorbing property was tested by a free space method in the microwave anechoic chamber.

Table 2
Compositions of the microwave absorbing paint

Composition	Content (g)
PS/Ag microspheres	16.8
Acrylics acid resin (R413B, from Dow Chemical, USA)	20
Defoaming agent (NXZ, from Napco, Japan)	0.2
Dispersing agent (5040, from Napco, Japan)	0.8
Film-forming agent (from Eastman, USA)	0.4
Water	61.2
Thickening agent (612NC, from Napco, Japan)	0.6

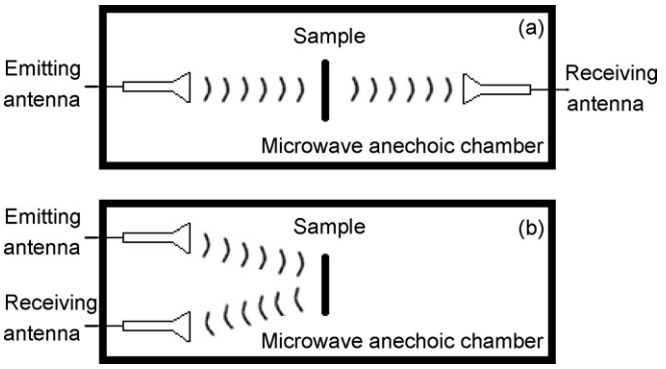

Fig. 1. The sketch maps of the measurement system. (a) Transmission attenuation and (b) reflection attenuation.

The distance between the emitting antenna (and receiving antenna) with the sample is far enough to content far-field condition. Before measurement, scaling was processed with an aluminum plate (100% reflector or 0% attenuation). The transmission and reflection attenuation were tested respectively by a microwave vector network analyzer. The sketch maps of the measurement system are shown in Fig. 1. Then the transmission and reflection ratio can be calculated by the transmission and reflection attenuation respectively. The impact intensity of the microwave absorbing coatings was tested based on the national standard of china GB1732-79. The adhesive force of the microwave absorbing coatings was tested based on the national standard of china GB1720-79. The flexibility of the microwave absorbing coatings was tested based on the national standard of china GB1731-79.

3. Results and discussions

3.1. Preparation of PS microspheres

The monodisperse PS microspheres with the average size of 1.6 μm were obtained by dispersed polymerization. SEM photograph of the polystyrene microspheres are shown in Fig. 2, which indicates that PS microspheres are spherical in shape and have smooth surface. It is known that, in general, the deposition reaction of the electroless silver plating occurs at the adsorbed catalytic active centers on the nonmetallic substrates. Subsequently, silver deposition continues autocatalytically. Activation was performed to adsorb palladium onto the PS surface, prior to plating. After pretreatment, the color of PS microspheres turned from white to

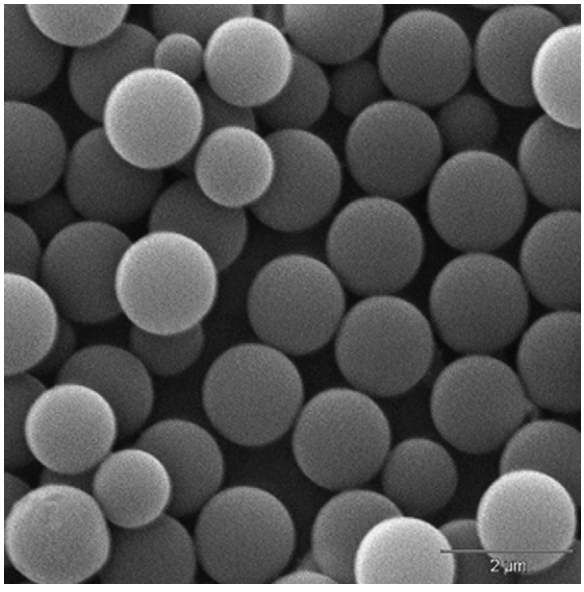

Fig. 2. SEM photograph of PS microspheres prepared by dispersion polymerization.