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Electromagnetic shielding effectiveness and mechanical property of polymer–matrix composites containing metallized conductive porous flake-shaped diatomite

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ABSTRACT

The porous flake-shaped diatomite particles with different micropores diameter were used as forming templates for the fabrication of the conductive core–shell functional fillers by electroless silver plating. The surface morphologies and phase structures of the surface coatings onto diatomite particles with different micropores diameter were evaluated. The effects of micropores diameter on electrical resistivity, electromagnetic shielding effectiveness and mechanical property of polymer–matrix composites containing silver-coated diatomite particles were also investigated in detail. The results show that the micropores onto initial diatomite particles after plating are completely covered with the coating, while the micropores onto diatomite particles with expanding pores are still visible. The expanding micropores onto diatomite particles in certain size range have less impact on the phase structures, electrical resistivity and electromagnetic shielding effectiveness. However, the mechanical properties of composites are improved significantly after expanding micropores by HF acid corrosion.

1. Introduction

In recent years, the usage of electronic and electrical devices has grown rapidly. The corresponding problem of electromagnetic radiation also becomes increasingly prominent. At present, electromagnetic radiation has become the fourth most serious source of public pollution in addition to noise, water and air pollution, which not only affect the normal work of the devices [1], but also hazard human health [2]. There is a growing need for suitable materials that will act as a shield and limit against the effects of electromagnetic radiation. The particle-filled (metal fillers, carbon fillers, etc.) polymeric composite structures are applied for electromagnetic shielding field to an increasing degree [3–10]. The objective is to obtain excellent electromagnetic shielding effectiveness and mechanical properties simultaneously to light weight. Furthermore, the related literatures reported that filler shapes and microstructures had significant effects on electromagnetic properties and mechanical properties as well, and flake-shaped particles were considered to be one of the most potential shielding fillers [11,12]. Ag powders were widely used as functional fillers for electromagnetic applications owing to their excellent electrical conductivity, and the flake-shaped Ag powders could be obtained by conventional processing method [13]. However, the primary defects of these fillers are high density and simple microstructures that cannot satisfy the comprehensive performances requirement of electromagnetic shielding composites.

In order to reduce the filler density and cut the costs, one preparation method of core–shell particles, *i.e.* depositing functional material on non-metallic powders (microspheres, fibers, carbon nanotubes, etc.) has been a hot research recently [14–19]. The electroless plating method is characterized in simple process and convenient operation, which is appropriate for core–shell particles preparation in large scale production [20–22]. Diatomite is a typical biological siliceous rock, which contains masses of frustules. It is formed by the action of the natural environment on remains of single-celled diatoms deposited on the sea bed, and inherits characteristics of shape and microstructure of diatoms. Diatomite not only has abundant and varied shapes including superior flake shape, but also has particular substructures such as porous and spinous [23,24].

Therefore, this paper attempts to fabricate porous flake-shaped particles by electroless silver plating on diatomite surface, and to investigate emphatically the effects of surface micropores on electrical resistivity, electromagnetic shielding effectiveness and mechanical properties.

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2. Experimental details

2.1. Materials

The diatomite particles used in this experiment are bought from Linjiang Sailite Diatomite Co., Ltd. The frustules in diatomite are mostly belonging to *Coscinodiscus* Ehrenberg which are gray–white and appear standard disc-shaped particles in general, as shown in Fig. 1. The overall characteristic parameters are as follows: diameter range of 20–50 μm, thickness range of 2–10 μm, specific gravity of 2.15 g cm^{-3}, main ingredient is SiO_2 (approximately 91 wt%), and lots of micropores distribute in the surface. Most of diatomite particles have separated into valves and girdle bands because of old age. Therefore, according to the method in the literature [25], the girdle bands were isolated from diatomite particles before they were taken as templates. Besides, in order to study the effects of surface micropores on electromagnetic shielding effectiveness and mechanical property, the micropores were expanded for different sizes by HF acid corrosion. The process parameters of HF acid corrosion were shown in Table 1.

2.2. Electroless silver plating

The surface activation method without using palladium salt was applied for electroless silver plating onto diatomite particles in this paper. The activated diatomite particles were put into the reducing agent solution, and then the silver–ammonia salt solution was added gradually. During the whole plating process, the mechanical stirring was used to avoid the agglomeration of diatomite particles and obtain uniform film onto them. The plating bath compositions and operation conditions were shown in Table 2. The coating thickness onto the diatomite particles is approximately 0.8–1.0 μm.

2.3. Morphology characterization

The morphologies of the coated diatomite particles were examined by an XSY-1 optical microscope with SONY DSC-H50 photographic camera and a scanning electron microscope (SEM, Cambridge CamScan CS3400). The composition analysis was made using an energy dispersive spectrometer (EDS, Oxford INCA). The crystal structures were characterized by employing the X-ray diffraction (XRD, Rigaku D/max-3) with Cu Kα radiation at a voltage of 40 kV, a current of 40 mA, step size 0.02°, scanning rate 8°/min and wavelength 1.5418 Å.

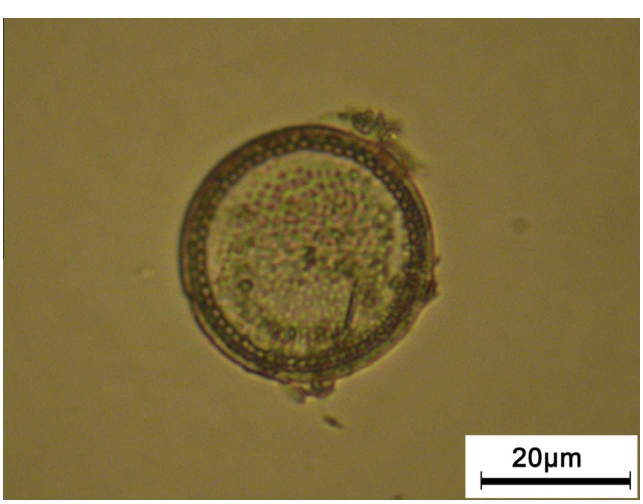

Fig. 1. Optical microscope image of diatomite particle.

Table 1
The process parameters of HF acid corrosion.

No.	Particles	HF concentration (%)	Corrosion time (h)
S-1	Diatomite	–	–
S-2	Diatomite	0.5	2
S-3	Diatomite	1	2

Table 2
The bath compositions and operation conditions.

Silver–ammonia salt solution		Reducing agent solution	
$AgNO_3$	15 g	$C_6H_{12}O_6$	22.5 g
$NH_3{\cdot}H_2O$	100 ml	$C_4H_6O_6$	2 g
NaOH	12 g	C_2H_5OH	50 ml
H_2O	500 ml	H_2O	500 ml
Time	15 min	Load	200 ml/g

2.4. Polymer–matrix conductive coatings

The silver-coated diatomite particles, polymer (polyurethane and silicon rubber), hardener, thinner and other additive were mixed in a certain proportion, and this mixture was stirred by high-speed dispersion machine for 30 min to make them more homogeneous. The type of substrate used in this paper was ABS circular plates, and their diameter was 115 mm. The ABS substrates were spray deposited with polymer–matrix conductive coatings for 80–100 μm in thickness, and then were placed in the air for curing at least 48 h.

2.5. Performance testing

The electrical resistivity measurements of polymer–matrix conductive coatings were carried out by a SZT-2A four-probe meter. The shielding effectiveness measurements were performed at the China Electronics Standardization Institute (CESI) using coaxial test systems, which consisted of an EMI receiver (ESCS30, Rohde & Schwarz) and a coaxial measurement instrument. The shielding effectiveness was assessed over 30–1500 MHz. The mechanical properties of shielding composites were measured by an electronic universal testing machine (Instron-5565) with tensile rate of 500 mm/min.

3. Results and discussion

3.1. Morphological properties

The surface morphologies of diatomite particles before and after expanding micropores by HF acid corrosion are shown in Fig. 2. It can be seen that the diatomite particles after HF acid corrosion keep their initial porous flake shape. In details, the sizes of the micropores onto S-1 initial diatomite particles are smaller and their pore diameters are about 160 μm. With the increase of the HF concentration, the sizes of the micropores onto diatomite particles are expanded significantly. The sizes of the micropores onto S-2 and S-3 diatomite particles with enlarged pores are approximately 315 μm and 600 μm.

The surface morphologies of diatomite particles after electroless silver plating are shown in Fig. 3. It can be observed that the diatomite particles after plating still keep their initial shape. As a whole, the surface coatings of the diatomite particles are homogeneous, continuous and compact, except for a small amount of tiny fragments. The electroless plating is a kind of method which can deposit the metallic coating on the surface of the non-metallic particles directly. During the electroless plating process, the diatomite