International Journal of Adhesion & Adhesives 48 (2014) 177–182

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

Surface functionalization of micro silver flakes and their application in electrically conductive adhesives for electronic package

Hui-Wang Cui [a,b,*], Qiong Fan [a], Dong-Sheng Li [a,b]

[a] Key State Laboratory for New Displays & System Applications and SMIT Center, College of Automation and Mechanical Engineering, Shanghai University, Shanghai 200072, China

[b] Institute of Scientific and Industrial Research, Osaka University, Ibaraki 567-0047, Osaka, Japan

ARTICLE INFO

Article history:
Accepted 19 August 2013
Available online 9 October 2013

Keywords:
Polymer-matrix composites (PMCs)
Surface functionalization
Electrical properties
Mechanical properties

ABSTRACT

In this study, we used 3-aminopropyltrimethoxysilane, hexanedioic acid, 3-mercaptopropyltrimethoxysilane, and thioglycolic acid to functionalize the surface of micro silver flakes through in-situ replacements. Hexanedioic acid had the best effect on the functionalization. When the content of hexanedioic acid was 0.5–1 wt% of micro silver flakes, it could fully replace the long chain fatty acid and form a very thin molecular film on the surface of micro silver flakes. The micro silver flakes functionalized by hexanedioic acid played a significant role in the regards of improving the properties of electrically conductive adhesives, and letting the adhesives have low viscosity, e.g., 28,000 cPs, low bulk resistivity, e.g., $2.4 \times 10^{-4}\ \Omega$ cm, and high shear strength, e.g, 10.4 MPa.

1. Introduction

How to improve the electrical and mechanical properties of electrically conductive adhesives (ECAs) has become an urgent issue in electronic package. Till now, many related methods have been reported. For example, increasing the curing shrinkage rate of matrix resin [1,2], in-situ replacing the surface lubricants on silver particles [3,4], sintering nano silver fillers at low temperature [5,6], and adding reductive agents [7,8] or low-temperature liquid fillers [9,10], etc., have been used to improve the electrical properties; and adding coupling agents [11–13], using matrix resin with low storage modulus [14–17], and reducing the amount of electrically conductive fillers [18,19] have been used to improve the mechanical properties. Micro silver flakes are the only industrial products among all of the electrically conductive fillers for ECAs. Their quality affects the properties of ECAs directly. Micro silver flakes are often functionalized using coupling agents, surfactants, and surface coating and grafting [20,21]. In this study, a simple in-situ replacement was introduced to functionalize micro silver flakes.

In our previous work [22–27], a matrix resin (containing a functional epoxy, a reactive diluent, a silane-coupling agent, and a curing agent) and a formulation of ECAs (25 wt% of matrix resin and 75 wt% of electrically conductive fillers) were obtained. These ECAs were cured at 150 °C for 30 min, had a high pyrolysis temperature above 350 °C and a high glass transition temperature around 180 °C. These matrix resin and formulation were used in this study. We firstly used 3-aminopropyltrimethoxysilane, hexanedioic acid, 3-mercaptopropyltrimethoxysilane, and thioglycolic acid to functionalize the surface of micro silver flakes through in-situ replacements, respectively. Then we incorporated the functionalized micro silver flakes into matrix resin to form ECAs. The functionalized micro silver flakes and their influences on the properties of ECAs were investigated.

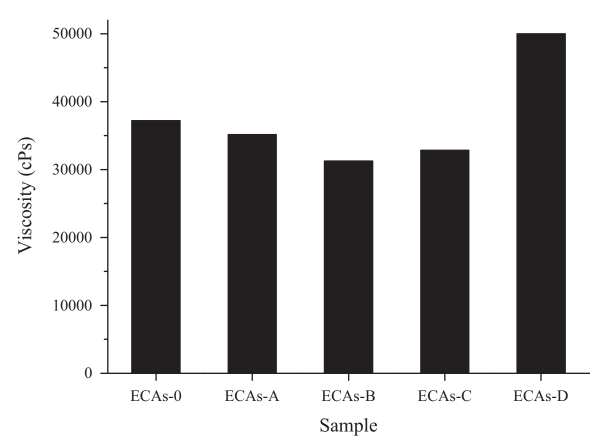

Fig. 1. Viscosity of ECAs.

* Corresponding author at: Key State Laboratory for New Displays & System Applications and SMIT Center, College of Automation and Mechanical Engineering, Shanghai University, Shanghai 200072, China. Tel.: +81 6 68798521; fax: +81 6 68798522.
E-mail address: cuihuiwang@hotmail.com (H.-W. Cui).

0143-7496/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijadhadh.2013.09.036

2. Experiment

2.1. Samples

In this study, the surface of micro silver flakes (size 5–10 μm, thickness about 0.5 μm) was coated by a long chain fatty acid (Sino-Platinum Co., Ltd., China). When used, these micro silver flakes were functionalized firstly using a simple in-situ replacement: the micro silver flakes, a functional agent, and anhydrous ethanol were mixed together and stirred vigorously for 12 h at room temperature; then the mixture was dried at 80 °C for 2 h and polished into powders. The functional agent was 1 wt% of micro silver flakes. The functional agents were 3-aminopropyltrimethoxysilane, hexanedioic acid, 3-mercaptopropyltrimethoxysilane, and thioglycolic acid, respectively (Sigma-Aldrich, USA). The functionalized micro silver flakes were noted as functionalized micro silver flakes-A, functionalized micro silver flakes-B, functionalized micro silver flakes-C, and functionalized micro silver flakes-D accordingly.

ECAs were composited of a matrix resin (25 wt%) and electrically conductive fillers (75 wt%). The matrix resin contained 74 wt% of functional epoxy (N,N-diglycidyl-4-glycidyloxyaniline,

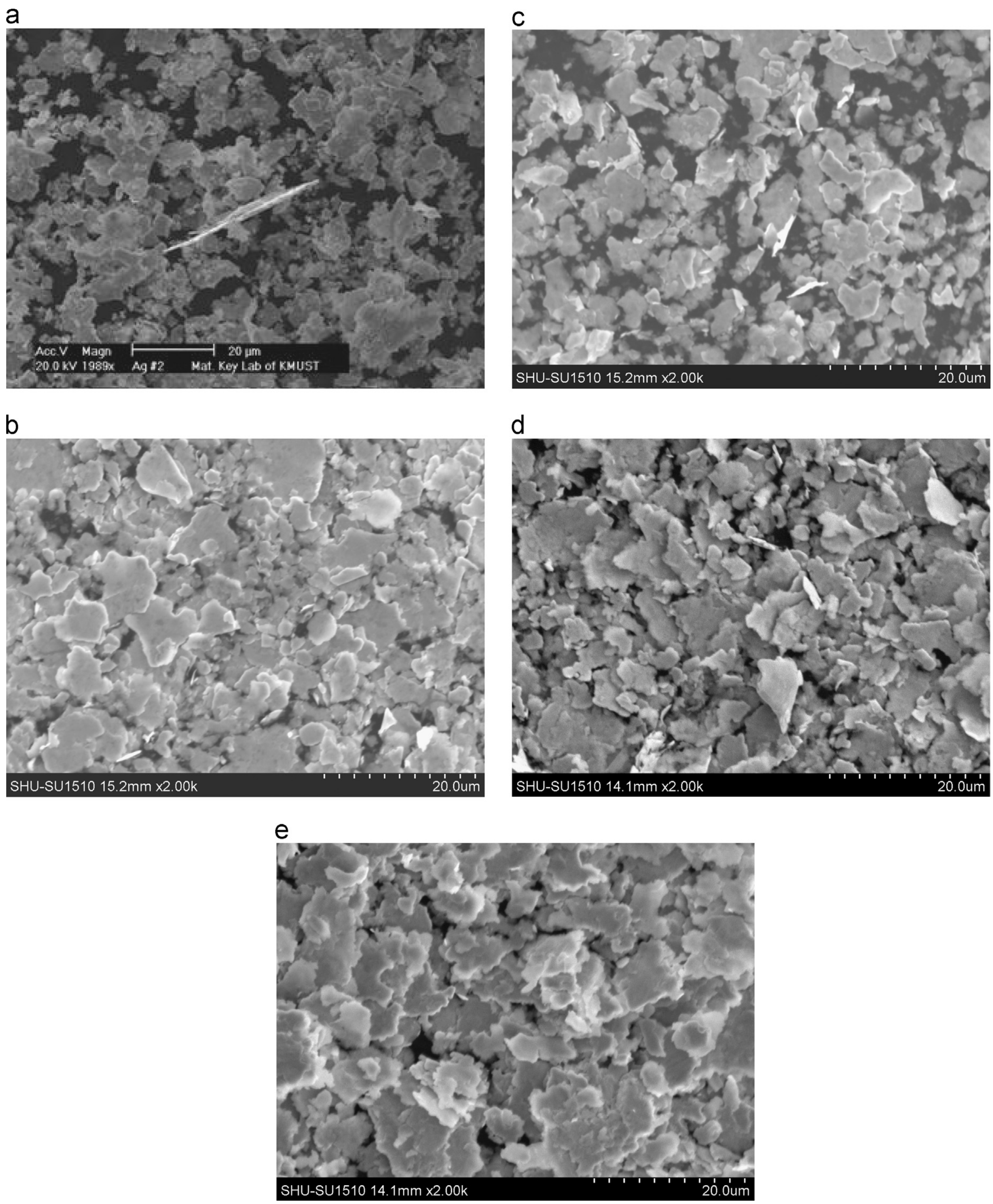

Fig. 2. Morphology of micro silver flakes. (a) Functionalized Micro Silver Flakes, (b) Functionalized Micro Silver Flakes-A, (c) Functionalized Micro Silver Flakes-B, (d) Functionalized Micro Silver Flakes-C and (e) Functionalized Micro Silver Flakes-D.