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CRACKING AND DELAMINATION OF NANOSCALE METAL COATING ON COMPOSITE POLYMER PARTICLES

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ABSTRACT

Metallized and monodisperse polymer particles in micron size are increasingly used in developing new electronic packaging technology, such as Anisotropic Conductive Adhesive (ACA). In this application, the large deformation of the particles is applied to increase the contact area and hence achieve a low resistance connection. Therefore mechanical properties of particles under large deformation are of crucial importance. Using a nanoindentation–based flat punch method, deformation and fracture of individual particles were systematically investigated with a wide range of test conditions. Through comparing the mechanical behaviour of individual metallized particles with uncoated ones, a significant strengthening effect of nanoscale Ni/Au coating on the deformation capacity of particles was discovered. A prominent increase in the stiffness of metallized particles was observed until the cracking and delamination of the metal coating. An interesting particle size effect was also discovered, which was dominated by the presence of the metal coating. These results provide essential knowledge for the design of metal coated polymer particles for different applications.

KEYWORDS

Metal coating; polymer particles; nanoindentation; flat punch; cracking; delamination

INTRODUCTION

Ugelstad monodisperse polymer spheres have been widely used in chemical industries and biotechnology [1]. Recently there is a growing interest in polymer spheres in microscale with ranging from 0.5 to 30µm with potential application in new electronic packaging technologies, such as Anisotropic Conductive Adhesives (ACA) in Flat Panel Displays [2]. By means of metallization of polymer particles, the particles become conductive and can be used in ACA assembly, schematically shown in Fig. 1. The metallized particles consist of a micron sized polymer core for improving contact compliance, a nanoscale Ni inner layer for obtaining electrical conductivity, and a nanoscale Au outer layer for protecting inner layer from oxidation and improving the reliability of electrical performance. The design of metallized polymer particles used in ACA technology possesses many advantages in terms of lead-free, reducing package size and achieving high-density interconnections. The mechanical performance of particles under large deformation is of crucial importance to a reliable connection. The failure of metallized polymer particles might bring a significant impact on electrical properties of the ACA assembly.

Due to the complexity of spherical shape and large deformation involved in the particles used in ACA assembly, mechanical characterization of individual particles is full of challenge. To cope with this problem, the authors developed a nanoindentation–based flat punch method for measuring the mechanical response of micron–sized polymer particles under

compression [3]. The contact load–displacement relationship, size effect and large deformation behaviour of individual polymer particles were investigated [4]-[6]. However, the metallized particles have a more complex structure. It is critical for the reliability of the ACA interconnect that the sphere including the metal coating is capable of withstand a large deformation during the bonding process. The aim of the present work is to study deformation properties of metallized particles and to understand the effect of nanoscale metal coating on the mechanical behaviour.

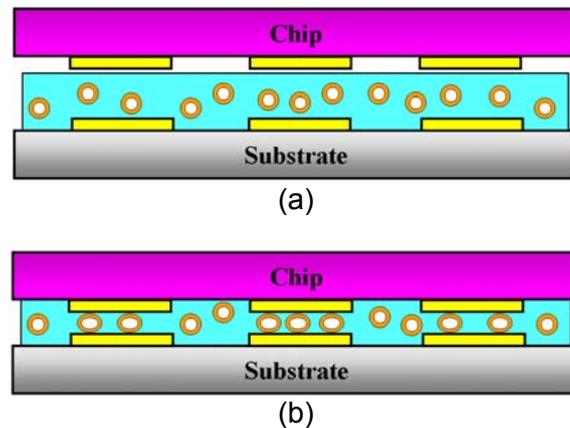


Fig. 1 A typical ACA assembly with metallized polymer particles: (a) before bonding and (b) after bonding.

EXPERIMENTAL

Materials

The commercially available acrylic copolymer particles (Concore™, Conpart AS, NO) were used as polymer core. The particles were made by Ugelstad method with a multi-step activated swelling process and were strongly crosslinked by 40% acrylic with 60% diacrylic. Two groups of the polymer core were sized of 3.8 and 4.8 μm , respectively. The C. V. (coefficient of variance) of size distribution was less than 2%, where C. V. was defined as the ratio of the standard deviation to the mean of particle diameter. The Ni and Au were deposited on the polymer core by an electroless plating process. The thickness of Ni inner layer and Au outer layer was about 50nm and 25nm, respectively. For comparison, uncoated particles with the same polymer chemistry and same size were also tested.

Due to the absence of surfactant, both dry and wet particles occur in a state of clusters. To obtain individual particles for the test, an efficient process of the sample preparation was developed. First a tiny amount of particles were immersed into 95% industrial ethanol, after redispersion in an ultrasonic vibration device, a small particle–ethanol suspension was dropped onto a silicon wafer with the size of 10mm \times 10mm \times 0.5mm. The specimen was left in a clean environment for 12 hours to dry any residual ethanol from the particles.

Apparatus

A nanoindentation device (TribolIndenter® Hysitron Inc., MN., USA) was employed to perform the mechanical testing of individual particles. The noise level of load and displacement were 100nN and 1nm in the current lab conditions. These values are obtained through the indentation in free air. A diamond flat–end punch of 100 μm in diameter, instead of a sharp tip

commonly used for nanohardness measurement, was designed for compressing individual particles, schematically shown in Fig. 2. A polished indium sample was used for the calibration of flat punch planarity and parallelism. An indent on a polished indium surface was used to assess the planarity of the flat punch as well as the relative positions of the integrated microscope and the flat punch.

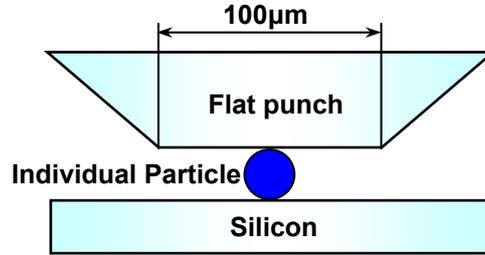


Fig. 2 Schematic plot of nanoindentation–based flat punch test with a flat tip of 100µm in diameter.

Method

Using the integrated optical microscope of Triboindenter, individual particles with more than 75µm distance to the closest neighbors can be easily identified. A three-step loading function was predefined for the mechanical test, including linear loading/unloading to/from the peak load and holding at the peak load segments. Five individual particles were tested for each set of experiments in order to check the repeatability of the results. A lot of experience in previous work has proven that the polymer particles from same batch behave very consistently [3]. This consistency indicates both a very homogeneous microstructure and an uniform size of the particles, as well as a reproducible experimental setup. The morphology of tested particles was observed using a scanning electron microscope (SEM) Zeiss Ultra 55 LE FESEM.

During compression the real time force and displacement on particles were monitored and the contact force–displacement curves were obtained. To compare the particle behaviour, the stress–strain relationship was calculated. Since the contact area between the particle and flat punch / silicon substrate was unknown, it was impossible to obtain the true stress–strain relationship of particles from the current experiment. Therefore the nominal compression stress–strain relationship of the particles was calculated using the follow equations:

$$\sigma_N = \frac{P}{\pi R^2} \quad (1)$$

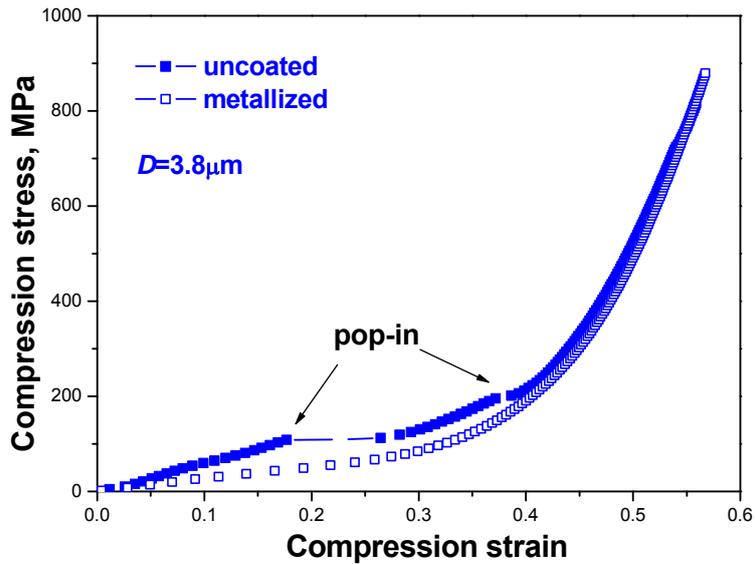
$$\varepsilon_N = \frac{D}{R} \quad (2)$$

where P was the applied force, D was the half displacement during compression and R was the radius of undeformed particle.

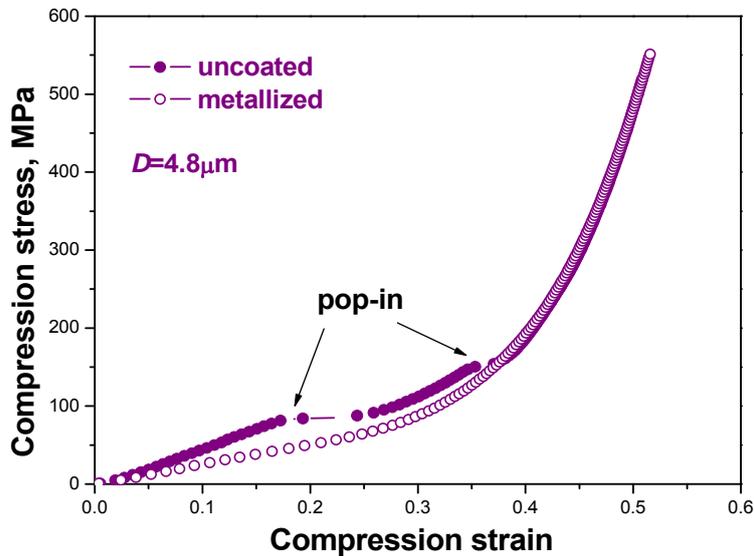
RESULTS AND DISCUSSION

The metallized and uncoated particles were compressed up to 10mN with linear loading/unloading rate 2mN/s and holding 2s at the peak load. The corresponding stress–

strain curves are shown in Fig. 3. The metallized particle sizes are 3.875 and 4.875 μm , respectively, while uncoated ones are 3.8 and 4.8 μm . Both 3.8 μm -based and 4.8 μm -based particles show similar behaviours. At the beginning of loading, the metallized particle is significantly stiffer than the uncoated one. The occurrences of a large “pop-in” at around 18% deformation on the loading segment suggest that a significant change has happened to the metallized particles. However, the metallized particle is still harder than the uncoated one, indicating that there are some mechanical integrity in the metal coating and adhesion to the polymer core left. With further deformation, one or more additional smaller “pop-ins” occurs, and finally the loading curves of the metallized and uncoated particles overlap each other. At this stage it is evident that the metal coating has no effect on the particle behaviour any more.



(a)



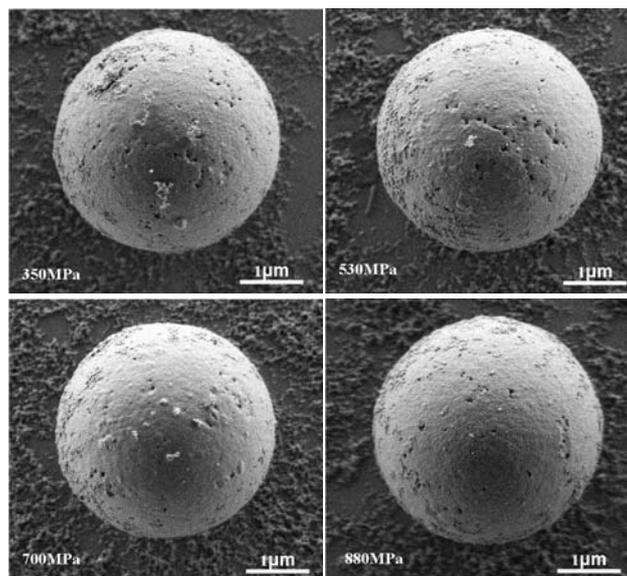
(b)

Fig. 3 The compression stress–strain curves of two groups of particles: (a) 3.8 μm particles and (b) 4.8 μm particles.

To clarify the pop-in mechanisms of the metallized particles, both metallized and uncoated 3.8 μm particles were compressed to different peak loads, namely, different stress level. The characteristic SEM images of particles under different stress levels are shown in Fig. 4. All images are taken from top view in the direction of the compression. In Fig. 4 (a), there is no cracking or failure observed on the uncoated particles. It is neither possible to observe any residual deformation or change in diameter of the particle after compression to the different stress levels. It indicates that the uncoated particle behaves viscoelastically and finally recovers completely within some time after unloading.

In Fig. 4 (b), the undeformed metallized particle shows that the metal coating is well plated on the core polymer particles. When the maximum stress is 80MPa, which is lower than pop-in stress level, the metallized particle shows a small flattened area which corresponds with the expected contact area under maximum deformation and indicates residual deformation in the metal layer. Increasing the maximum stress up to 160MPa and 250MPa, cracking and delamination are clearly shown and aggravated with increasing stress. At 160MPa stress, cracking of the metal is observed while both cracking and delamination are shown in the image corresponding to the particle compressed to 250MPa. The crack propagation is along the longitudinal direction of the particles, and the delamination usually occurs underneath the cracks. The fragments induced by the cracking and delamination were measured in SEM. The thickness of fragments is in a range of 70 to 80nm, which agrees with the coating parameter during coating plating. That indicates that the delamination happens at the metal–polymer interface but not Ni–Au interface. There is a weaker adhesion at the metal–polymer interface than that at Ni–Au interface in the metallized particle.

Through comparing the stress–strain relationships of metallized particles and uncoated particles, the effect of the Ni/Au coating is disclosed. According to the metal coating effect, three stages could be identified in the deformation process of metallized particles. Initially, the Ni/Au coating has a significant strengthening effect thus the metallized particle is harder than the uncoated counterpart. Secondly, the effect of the metal coating is significantly reduced when cracking and delamination of the metal coating occur. The critical deformation for the failure of the metal coating for these metallized particles is found to be around 18%. Finally, the mechanical strengthening effect of the metal coating disappears completely and the metallized particle shows nearly identical behaviour as the uncoated one when the deformation is over about 43%.



(a)

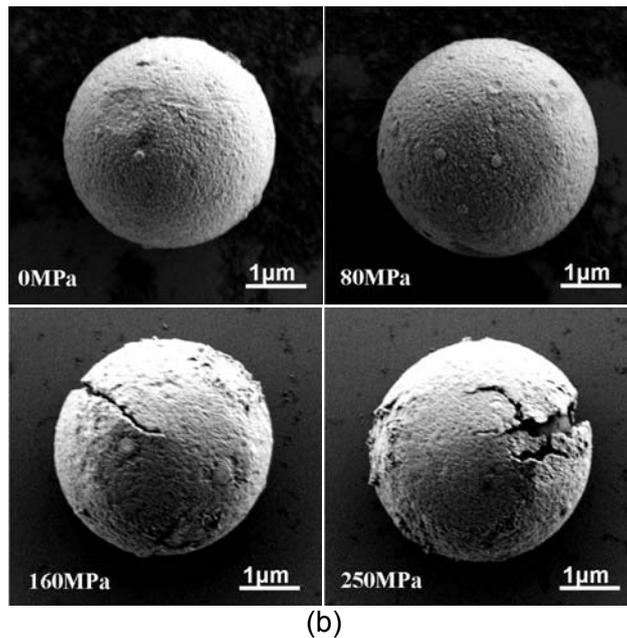


Fig. 4 The SEM images of particles at different stress level (a) uncoated particles and (b) metallized particles.

The stress–strain relationship of two metallized particles is compared in Fig. 5. The pop-in on both particles occurs at around 18% deformation. A particle size effect can be clearly observed, which shows that the 3.8µm particle is harder than the larger 4.8µm particle. This is consistent with the previous finding on polystyrene-divinylbenzene (PS-DVB) copolymer particles [4]. The size effect of PS-DVB particle is mainly contributed by a “core–shell” structure where there is a higher crosslink density in the surface shell than the core due to different hydrophilicity of DVB and styrene monomers. In this work, the presence of the metal coating significantly influences the particle behaviour and it is clearly the mechanism for the particle size effect. Since the metallized particles have different core size but same coating thickness, the volume fraction of the metal coating in two metallized particles are different. This results in the particle size effect.

To understand this effect, finite element analyses were carried out to estimate the metal coating influence on the size effect using ABAQUS. The linear elastic material was assumed and axisymmetric elements were used to model the particles. Axisymmetric analytic rigid surface was used to model the diamond flat punch. The particle core has a diameter of 3.8µm and 4.8µm, deposited by the metal coating with same thickness 75nm. The assigned Young’s moduli for the metal coating and polymer core were 200GPa and 1.5GPa, and the Poisson’s ratios were 0.31 and 0.33, respectively. The interface between metal and polymer was assumed to be perfect adhesion due to the lack of a fracture criterion. The finite element solutions of metallized particles and uncoated particles are shown in Fig. 6. Metallized particles are much stronger than uncoated ones, in agreement with experimental results. Two uncoated particles behave identical while metallized particles display a particle size effect that the smaller particle is harder, which is consistent with experiment. This demonstrates that the metal coating plays a dominate role on the particle size effect.

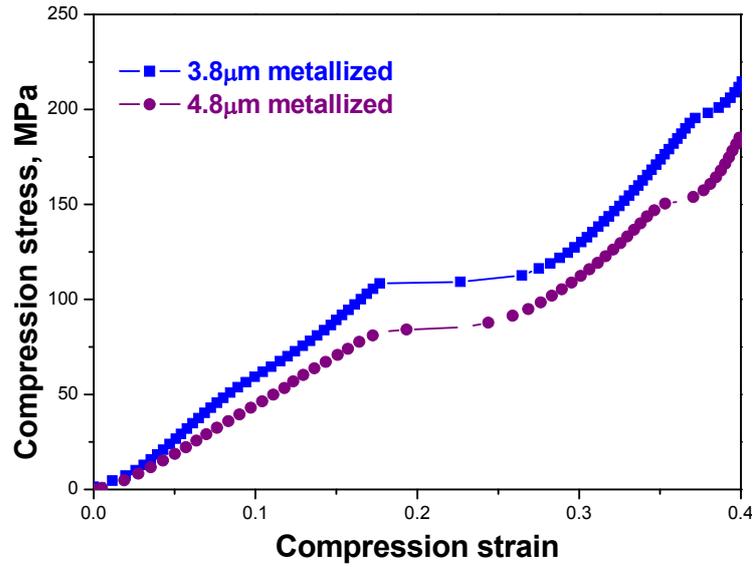


Fig. 5 The stress–strain relationship of metallized particles.

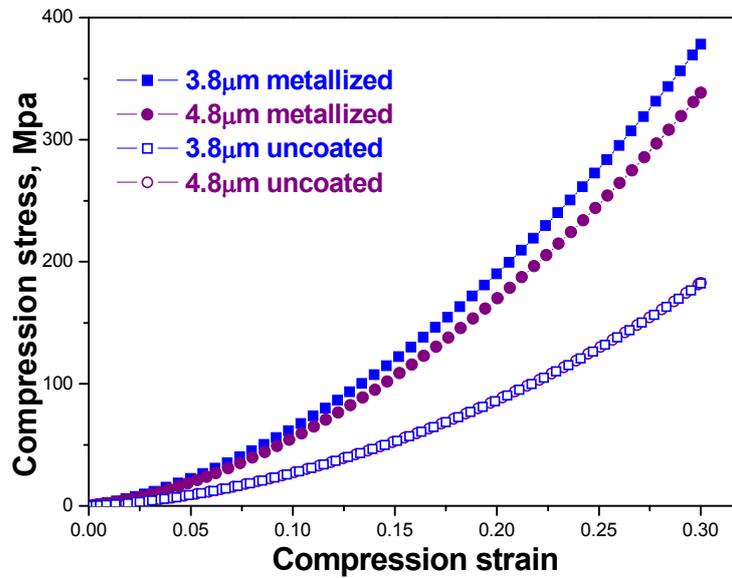


Fig. 6 Finite element solutions of metallized and uncoated particles.

CONCLUSIONS

The mechanical behaviour of both Ni/Au coated and uncoated acrylic particles was studied by using the nanoindentation–based flat punch method. The Ni/Au coating was shown to play a significant strengthening role on particle deformation behaviours. The cracking and delamination of the metal coating was observed at a deformation level of 18%. According to the metal coating behaviour, a three–stage deformation process of metallized particles was identified through comparing the stress–strain relationship of metallized particle to that of the uncoated counterpart. A size effect of metallized particles was discovered and the finite element solutions demonstrated that the metal coating was the dominating factor to the

particle size effect. The findings have important implications in the design of the metallized polymer particles for electrical packaging applications.

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