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Characteristics of Graphene-Filled Solderable Isotropically Conductive Adhesive (ICA)

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A new class of functionalized graphene-filled solderable isotropically conductive adhesive (ICA) has been developed using a low-melting-point alloy (LMPA) fillers. The mechanical and electrical characteristics of formulated ICAs were investigated and compared with those of three kinds of conventional ICAs filled with Ag particles. The functionalized graphene-filled solderable ICA formed good metallurgical interconnection between upper and corresponding lower electrode. The developed ICA exhibit lower electrical resistance and higher mechanical strength compared with those of conventional ICAs. In addition, the thermal conductivity was improved about 20% by adding functionalized graphene compared with that of solderable ICA without graphene. [doi:10.2320/matertrans.M2011365]

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1. Introduction

Graphene has been received tremendous attention in recent years due to their exceptional thermal, mechanical, and electrical properties.[1)] A suspended graphene sheet could exhibit extremely high thermal conductivity values ranging from $(4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$ W/mK.[2)] The theoretical elastic and young modulus of single graphene sheet are about 1 TPa and 1060 MPa, respectively.[3)] It also has an excellent electrical property with a surface conductivity of 50×10^6 S/cm. Owing to these potential advantages, graphene is considered to be one of the strong candidates for a filler material in reinforced composites.

The conductive filler-filled polymeric composites have been widely used for a wide range of applications, due to their versatile properties, such as thermal stability, mechanical response, electrical resistance and adhesive characteristics.[4)] Among them, isotropically conductive adhesives (ICAs) filled with organic or inorganic fillers have been actively investigated, due to their potential advantages such as lower temperature processing, more flexible and simpler processing, and compatibility for nonsolderable materials.[5)] However, there are several critical limitations such as lower conductivity, unstable contact resistance with non-noble metal finished components, and poor mechanical performance compared with traditional solder material.[6,7)] Some researchers reported that the electrical properties of ICAs could be improved by adding low-melting-point alloy (LMPA).[8,9)] In our previous work, it was proved that LMPA is effective filler material to improve the electrical and mechanical properties of ICAs.[10,11)] In this paper, a new class of functionalized graphene-filled solderable isotropically conductive adhesive (ICA) is presented. The influence of graphene on mechanical, electrical and thermal properties of assembly was investigated.

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Table 1 Components of ICA formulations used.

ICA	Polymer	Filler
ICA 1	Epoxy-type (W/O functionalized graphene)	Sn-58Bi (40 vol%)
ICA 2	Epoxy-type (With functionalized graphene)	Sn-58Bi (40 vol%) + GO (1 mass%)
ICA 3	Epoxy-type	Ag flake
ICA 4		
ICA 5	Polyester-type	

2. Experimental

The developed ICA consists of a graphene oxide (GO), LMPA, a thermoset polymer resin and other minor organic additives. GO was synthesized using the modified Hummers method.[12)] A diglycidyl ether of bisphenol A (DGEBA; Kukdo Chemical; epoxy equivalent weight (E.E.W.) = 186.8 g/eq) was used for the binder, and 4,4′-diaminodiphenylmethane (DDM), prepared by TCI Korea, was used as a curing agent. The LMPA solder ball (Sn-58Bi; $T_m = 412$ K; 45 μm) was obtained from Senju Industrial Company. 3-butanoic acid (Aldrich, 97%) was used as a reductant to remove the oxide layer from the surfaces of the LMPA and the conductive pad.

To compare mechanical and electrical properties, two kinds of ICAs with and without GO were formulated and compared with those of three kinds of conventional ICAs filled with Ag particles. Thermal conductivity of ICA with and without GO was determined using a Netzsch 457 laser flash analysis (LFA) instrument. Samples were cut into 10×10 mm bars. A total of 5–10 shots were taken per sample set. The ICA formulations are shown in Table 1. For an adhesive bonding test, the quad flat package (QFP) with 44-pin I/O terminals plated with Sn ($14 \times 14 \times 2.7$ mm^3 in size, and 1.0 mm in lead pitch) and 18 μm thick Cu plated printed circuit board (PCB) ($32 \times 32 \times 1.0$ mm^3) were used.

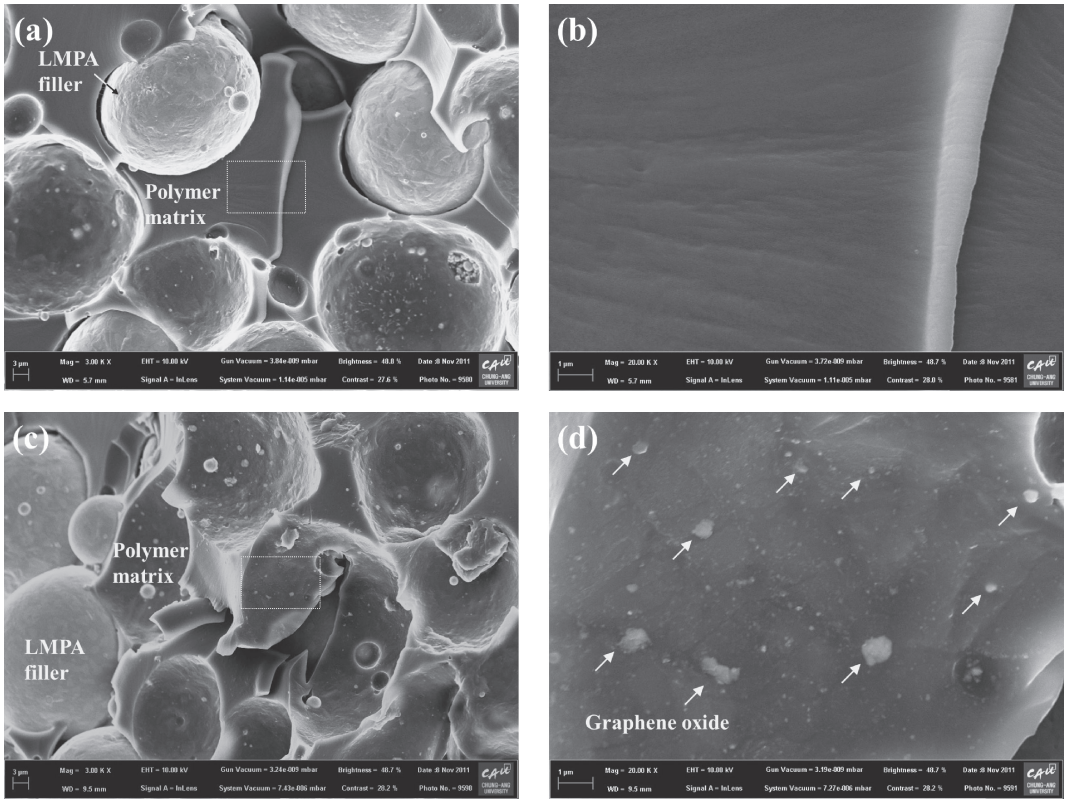

Fig. 1 FE-SEM images of solderable ICAs (a) w/o GO at low magnification, (b) w/o GO at high magnification, (c) with GO at low magnification, and (d) with GO at high magnification.

The substrate was cleaned with acetone for 1 min, rinsed with DI water and dried with an air jet. ICAs were selectively applied on the conducting pads by screen method. QFP was then aligned on the PCB, and adhesive bonding was conducted by using chip bonder (LAMBDA: FINETECH Co.). After the adhesive bonding, the electrical property was investigated through a daisy-chain connected probe terminal by using a multi-meter (34410A: Agilent Tech.). The morphology of the conduction path was observed by the optical microscope (VHX-100: KEYENCE Co.). To observe the mechanical property of each ICA joint, the 45 degree pull test (JIS Z 3198-6) on QFP lead was performed. The QFP lead was pulled upward at 6 mm/min and the total number of leads being pull tested was 22 for each ICA assembly.

3. Results and Discussion

Figure 1 shows the microstructures of ICA without and with functionalized graphene (1 mass%). The surface exhibited dispersion and compatibility of LMPA and functionalized graphene in the epoxy resins. The FE-SEM images of ICA containing functionalized graphene showed that the distribution of functionalized graphene fillers was uniform without segregation after curing [Figs. 1(c) and 1(d)]. The good distribution of functionalized graphene in epoxy could be attributed to the intermolecular interactions between the epoxy matrix and the fillers, such as intermolecular hydrogen bonding between the hydroxyl group in the epoxy and the hydroxyl group in the filler surface.[13,14)]

Figure 2 shows the morphology of the conduction path of each formulated ICA. The interconnected parts were divided into two distinct regions. One is a conductive path made by melted fillers, and the other is a polymer wrapped around the outside of the conduction path. The white dotted line shows the cured polymer region. As can be seen in the images, the formulated ICAs with LMPA showed a good reduction capability and the LMPA fillers were mostly wet and metallurgically interconnected between the metallizations of the QFP lead and substrate, regardless of the existence of functionalized graphene. The spherical LMPA fillers remained outside the interconnection region. Since the remaining LMPA fillers were covered with the polymer matrix, the QFP assembly maintained its insulation properties between adjacent leads.

Figure 3 shows the electrical resistance of the QFP assemblies using each ICA. Graphene-filled solderable ICA 2 showed an almost same level to ICA 1 without functionalized graphene and much lower electrical resistance (1.93 Ω) than those of other conventional ICAs (8.69 Ω for ICA 3, 4.96 Ω for ICA 4, and 7.82 Ω for ICA 5). This was due to a stable electrical conduction path caused by sufficient wetting, and the coalescence behavior of the LMPA fillers in ICA 2 during the curing process.

Figure 4 shows the results of the pull test of the QFP assemblies with each ICA. The QFP assembled with functionalized graphene-filled ICA 2 exhibited almost same level ICA 1 without functionalized graphene (18.38 N) and excellent pull strength properties. Its pull strength was 17.73 N, which was more than three times greater than the

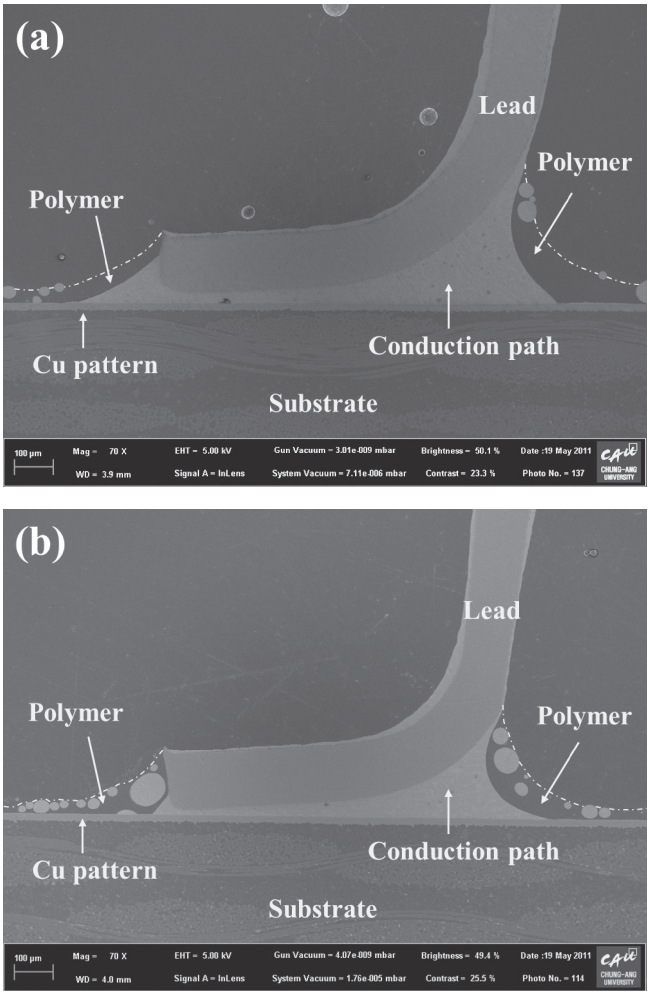

Fig. 2 Morphology of the conduction path formed between metallizations of QFP and PCB substrate by using solderable ICA (a) w/o GO and (b) with GO.

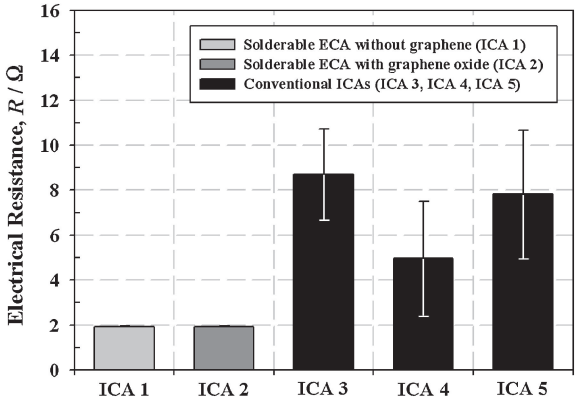

Fig. 3 Electrical resistances of QFP assemblies.

QFP assemblies with conventional Ag-filled ICAs (ICA 3, ICA 4, and ICA 5). This was due to the robust interconnection achieved through metallurgical bonding between the metallizations of the chip and substrate.

Figure 5 compares the thermal conductivities of ICAs with and without functionalized graphene. The graphene-based materials provide and efficient thermal conductivity enhancement compared to those of other carbon materials, because of

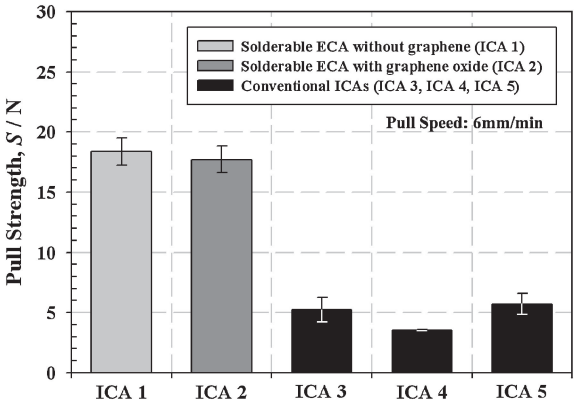

Fig. 4 Pull strengths of QFP assemblies.

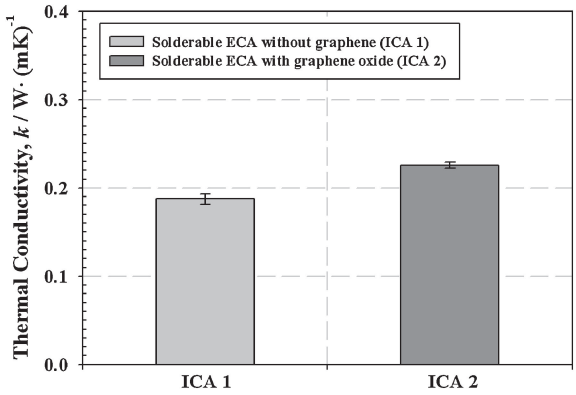

Fig. 5 Thermal conductivities of QFP assemblies.

the high aspect ratio, dimensionality, rigidity of the graphene layer and the thermal interface resistance between the graphene and polymer matrix.[15] The thermal conductivity of the ICA 1 without functionalized graphene was around 0.188 W/mK and the thermal conductivity of the ICA 2 was increased to about 20% (0.225 W/mK).

4. Conclusion

A novel graphene-filled solderable ICA with LMPA was developed. The morphology of the achieved conduction path, which was formed by the flow-coalescence-wetting behavior of LMPA fillers in the ICA, was investigated. The effects of functionalized graphene sheets within ICAs with LMPA on the electrical, mechanical and thermal properties were investigated. The dispersion of functionalized graphenes in the polymer matrix was good, and the stable metallurgical interconnection caused by the flow-coalescence-wetting behavior of LMPA fillers in the ICA resulted in good electrical and mechanical properties, compared to conventional ICAs with Ag flake. Further, the thermal property can be enhanced by adding functionalized graphene.

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