450% THERMAL-CONDUCTIVITY INCREASE IN SILVER-FILLED EPOXY RESINS LOADED WITH CARBON NANOTUBES AND GRAPHENE

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Abstract

Silver-filled epoxy resins, such as the EPO TEK H20E (a standard for high speed chip bonding), feature remarkable thermal conductivity (~ 2.5 W/mK) and low electrical resistivity (~ 4×10^{-4} ohm-cm) characteristics, thanks to the presence of micrometric metallic particles embedded in the epoxy matrix.

Here we show that the addition of Carbon Nanotubes (CNTs) and Graphene nanoplatelets (GNPs) allows to improve by a factor ca. 5 the conductivity properties of the EPO TEK H20E reaching optimal values of 11.15 W/mK and 8×10^{-5} ohm-cm for the thermal conductivity and the electrical resistivity, respectively, without compromising the other performance aspects of the polymers.

1. Introduction

The development of high-conductivity adhesives represents an essential technological step for the fulfillment of present and future needs in packaging systems for electronic and high power microwave devices [1]. Inclusion of micro-structured metallic fillers into the epoxy matrix yields electrically conductive adhesives with volume resistivity down to 10^{-4} Ω-cm and the thermal conductivity of some W/mK [2]. CNTs have excellent electrical [3] and mechanical properties [4] that can be readily transferred to make electrically conductive [5] , strongly reinforced nanocomposites [6.7]. Transmitting the thermal properties (conductivity up to 3500 W/mK) [8] to polymeric materials is, however, still a challenge. Processes underlying thermal conductivity enhancement are more subtle than the percolation phenomena ruling electrical conductivity increase [9]. In particular, the CNT-polymer interface thermal resistance plays a role, limiting the maximum conductivities to 0.3-1 W/mK [10-14].

Also, GNPs is predicted to have remarkable properties, such as high thermal conductivity, superior mechanical properties and excellent electronic transport properties.

Graphene fillers have been successfully dispersed in poly(styrene) and epoxy matrices [18-20]. Rafiee et al, [21] show that at low nanofiller content graphene platelets perform significantly better than CNTs in terms of enhancing of mechanical properties, due to enhanced specific area of graphene platelets.

Here we show that addition of CNTs to silver-filled epoxies yields nanostructured glues with average (maximum) thermal conductivity of 8.8 W/mK (10 W/mK), tripling of the conductivity of the pristine resin with CNTs loads as low as 1% w/w. Indeed, also the samples loading with 6wt% GNPs shows the thermal conducibility of 11.15 W/mK.

To this aim, we have set up an effective method for dispersion into the metal-filled epoxy resins of carbon nanofillers of different nature (CNTs and GPNs). The resulting glue features a four times enhanced electrical conductivity (9.5×10^5 S/m, with maximum observed values of 1.2×10^6 S/m). Scanning Electron Microscopy provide insight on the crucial role played by the CNTs and GPNs in bridging together the silver micro-particles through the epoxy matrix, filling and reinforcing the structure of the nanocomposite material, at the same time.

1.1 Experimental

Epoxy Resin (EPO-TEK H20 E PART A) and hardener (EPO-TEK H20 E PART B) were based on glycidyl ether of novolac and modified amine, respectively.

EPO TEK H20E is two components system, containing approximately 78%w/w silver in the range from 1 to 10μm in size, and appear to be flat platelets [riferimento] and for this reason is used in microelectronic and optoelectronic applications also due to its high thermal conductivity.

Double Carbon Nanotubes (CNTs) used in this study were supplied by NanoLab. The CNTs were made via chemical vapor deposition (CVD), with a purity of 99,5%. The average diameter and length of the CNTs were 1±4 nm and 1/5 μm, respectively. Natural graphite flakes with an average diameter of 150 micron supplied form Graphene Supermarket.

CNTs and GPNs tend to aggregate into ropes or bundles due to the strong intrinsic Van der Waals forces and the inert graphite-like surface, causing poor dispersion in polymer matrix. For this reason the quality of nanofiller dispersion in the polymer matrix directly correlates with its effective ness for improving mechanical, electrical, thermal, impermeability and other properties.

Isopropyl alcohol was used to decrease the viscosity of the epoxy resin and to facilitate the carbon nanostructures (CNTs and GPNs) dispersion in the matrix. So, in the first time the

Next, the resultant mixture of carbon nanofiller epoxy was heated for 1h at 70 °C to remove residual Isopropyl alcohol.

Finally, the nanocomposites (CNTs/epoxy and GNPs/epoxy) is cured for 1h at 80°C, in accordance to the epoxy manufacturer's guidelines.

The thermal conductivity was measured using a Hot Disk Thermal Analyser (Hot Disk AB, Uppsala/Sweden), which is based upon a transient technique. A minimum of eight individual measurements was performed on four different samples for each various DWCNTs weight contents (from 1% up to 4%). The sensor (3 mm diameter) supplied a heat-pulse of 0.03 W for 20 s to the samples and the associated change in temperature was recorded. Every measurement was performed at room temperature.

The electrical conductivity of the nanocomposites were measured by a digital multimeter DMM2002 of Keithley.

The morphology of the samples was investigated by using a high brilliance LEO 1530 (FE-SEM) apparatus. The samples have been graphite-coated in order to avoid charging effects. The coating was deposited by using a sputter coater unit at a pressure of $1 \times 10\text{-}5$ mbar in order to produce a carbon film with a nearly constant thickness less than 1.0 nm.

1.1.1. Result

The thermal conductivity of epoxy composites with carbon nanofillers was measured by a hot disk thermal conductivity analyzer at room temperature. Thermal conductivity is affected by the carbon nanofillers structure quality within the matrix, loading, dispersion, and the thermal resistance of the interface between nanofillers and the polymer matrix.

Fig.1 shows the thermal conductivity of pristine epoxy, epoxy/CNTs composites and epoxy/GNPs composites, respectively.

The thermal conductivity of the pure epoxy resin is around 2.5 W/m K. The thermal conductivity of the epoxy resin changed with the addition of carbon nanofillers. At 1wt% CNTs loading, the thermal conductivity increases from 2.5 to 8.8 W/m K. As the nature of filler changed, the thermal conductivity increases . Indeed the thermal conductivity of GNPs composites is 11.15W/mK

There are several possible reasons for this, which include enhanced specific area of graphene platelets.

Indeed, the increased thermal conductivity is ascribed to the formation of a more efficient percolating network with significantly reduced thermal interface resistances.

As expected, the electrical conductivity of the epoxy resin is increased by a few orders of magnitude when the nanofillers are embedded in epoxy resin, which suggest that also in this case the carbon nanostructures provides a more efficient percolating network.

As well known, also electrical properties of the nanocomposites with fillers depend on the microstructures such as dispersion state, filler geometry and content, as well as filler-filler interaction.

Figure 2 shows the electrical resistivity of the nanocomposites as a function of the nanofillers. These result indicates that the dispersion level of GNPs appears to be slightly improved if compared with other nanocomposites, which should be responsible for the lower resistivity obtained in the GNPS nanocomposites (Fig2).
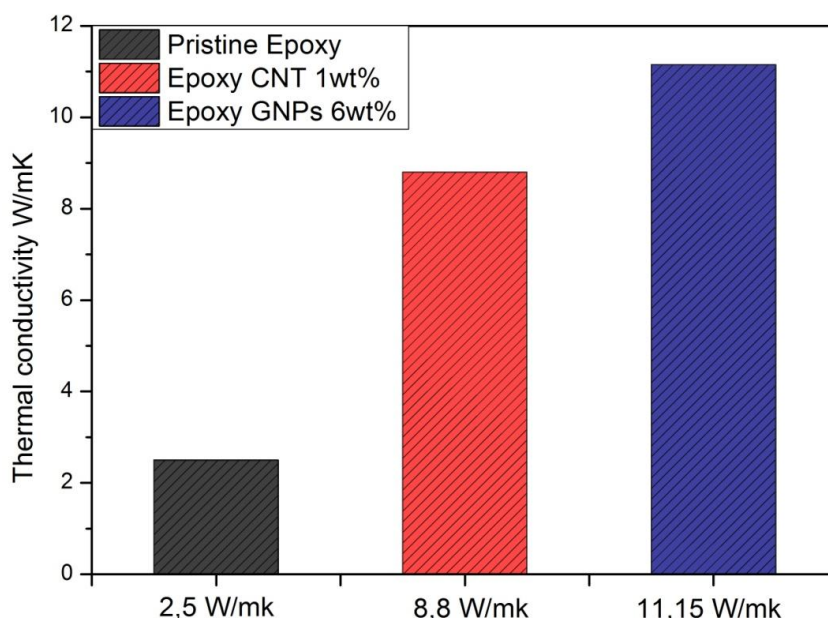
Figure 1. Thermal conductivity of epoxy composites with 1wt% CNYs and 6wt% GNPs

The quality of dispersion will be verified by using SEM (Fig 3). The fracture toughness of polymers, tantamount to an improved resistivity against crack propagation, thus a higher damage tolerance, is a crucial and limiting factor for the design of structural components, especially with regard to the long-term behavior. Therefore, an improvement of the fracture toughness of epoxies is a desirable goal of research activities.

Figure 3 shows a typical overview on the fracture surfaces of neat epoxy, composite containing 1 wt % CNT, and 6 wt% GNPS, respectively. SEM image clearly shows that in a both case an even dispersion of carbon nanostructures is achieved throughout the epoxy matrix.
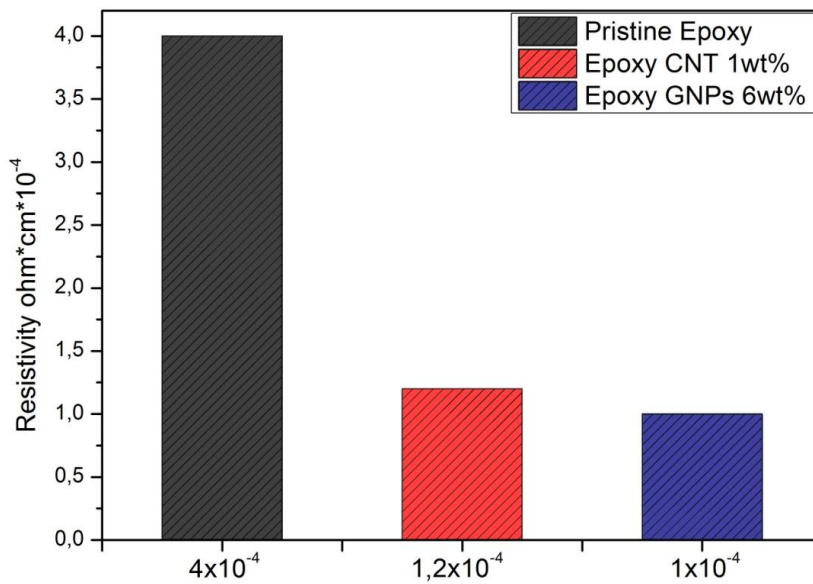

Figure 2. Resistivity of epoxy composites with 1wt% CNYs and 6wt% GNPs
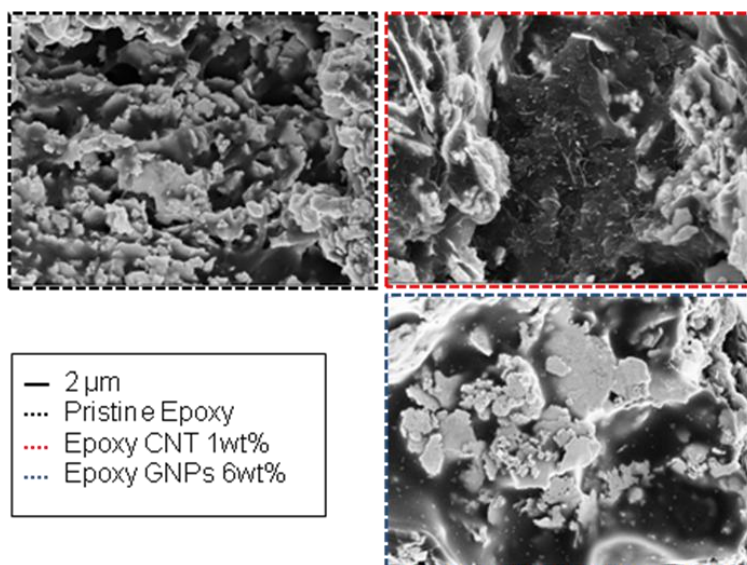

Figure 2. Resistivity of epoxy composites with 1wt% CNYs and 6wt% GNPs

1.1.1.1. Conclusion

In summary, we show that at low nanofiller content GNPs and CNTs perform an enhancing a variety of properties including thermal and electrical conducibility.
This approach is promising for large-scale production of highly conductive metal-carbon nanostructured epoxy adhesives at low cost, suitable for chip bonding when high power dissipation is a concern.

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