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Carbon nanotubes and silver flakes filled epoxy resin for new hybrid conductive adhesives

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A B S T R A C T

Combining conductive micro and nanofillers is a new way to improve electrical conductivity. Micrometric silver flakes and nanometric carbon nanotubes (CNTs) exhibit high electrical conductivity. A new type of hybrid conductive adhesives filled with silver flakes and carbon nanotubes (DWCNTs or MWCNTs) were investigated. High electrical conductivity is measured as well as improved mechanical properties at room temperature. Small agglomerates and free MWCNTs dispersed in the silver/epoxy composites improve the electrical conductivity and a synergistic effect between MWCNTs and micro sized silver flakes is observed in hybrid composites. Glassy and rubbery storage moduli of the hybrid composites increase with increasing silver loading at fixed CNTs volume fraction. High value of the storage modulus, measured in DWCNTs/μAg hybrid composites at rubbery state, is caused by strong agglomeration of DWCNTs bundles. The electrical and mechanical properties are consistent with the morphologies of the hybrid composites characterized by SEM.

1. Introduction

Electrical and thermal conductive adhesives used for the assembly of electronic devices (from digital to microwave applications) on various substrates (metallic packages, multichip modules, printed circuit boards) are silver particles filled. Micrometric silver flakes are dispersed in polymer matrix at very high filler concentrations (more than 25 vol%) to obtain sufficiently high electrical and thermal conductivities but associated with poor mechanical properties.

Compared to silver flakes, carbon nanotubes (CNTs) are well known to exhibit very low percolation thresholds in epoxy matrix [1] and intrinsic electrical [2,3] and thermal [3,4] conductivities at the same order than metallic nano or microparticles.

Recent literature and patent reviews show the growing interest of hybrid filler for thermally and/or electrically conductive adhesives [5–7]. This new type of filler combines the very high electrical and thermal conductivities of both silver flakes (σ = 6.10^7 S m^{-1}; λ = 426 W m^{-1} K^{-1}) [8] and carbon nanotubes (σ = 1.10^4–2.10^5 S m^{-1} [9]; λ = 200–3500 W m^{-1} K^{-1} [3,10–14]). Moreover CNTs have very high aspect ratio and therefore one can expect to elaborate hybrid CNTs/silver flakes composites with high electrical conductivities and lower silver content than usual silver filled adhesives.

2. Materials

A commercially available epoxy matrix was supplied by SIQ Company (Germany). The resin SIQ FP 113 was used as prepolymer and the SIQ FP 403 as hardener. Compared to others commercial available epoxy matrixes, SIQ resin has a low viscosity of 0.46 Pa s at room temperature, suitable for highly filled composites.

Two types of CNTs have been used. Double-wall carbon nanotubes (DWCNTs) were synthesized by CCVD in CIRIMAT [15]. Statistical studies on HRTEM images of 206 carbon nanotubes showed that more than 70% are DWCNTs with an average outer diameter of 2.4 nm (Fig. 1). The DWCNTs aspect ratio was estimated to be about 3500. CVD multi-wall carbon nanotubes (MWCNTs) were supplied from Future Carbon (Germany). A HRTEM study showed that more than 68% of 113 CNTs have between 5 and 10 walls and an average outer diameter of 11.7 nm (Fig. 2). The MWCNTs aspect ratio was estimated to be about 170. The main characteristics of both types of CNTs are summarized in Table 1. Density was calculated according to [16]. Specific surface area was determined from BET method.

Silver flakes AX20LC were supplied by Amepox (Lodz, Poland) with a purity of 99.99% and an average diameter of 3 μm.

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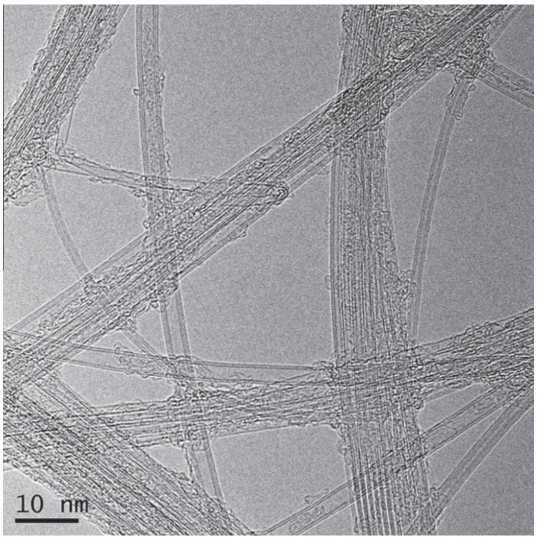

Fig. 1. HRTEM image of CNTs from CIRIMAT.

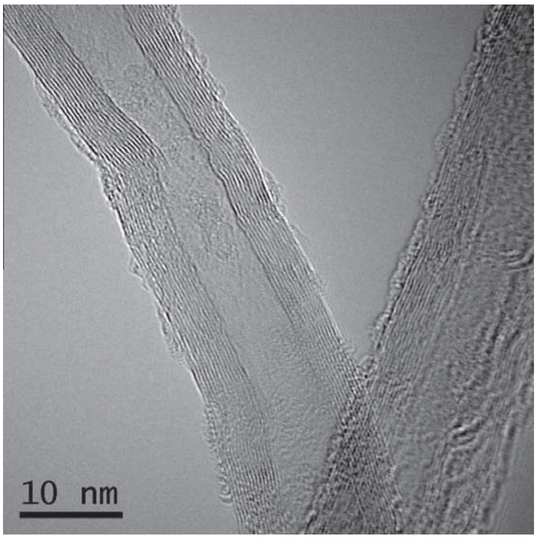

Fig. 2. HRTEM image of MWCNTs from future carbon.

Table 1
Characteristics of DWCNTs and MWCNTs.

	DWCNTs	MWCNTs
Number of walls	2	5–10
Diameter (nm)	2,8	11,7
Length (μm)	≈10	1–2
Aspect ratio	≈3500	85–17
Density (g cm^{-3})	2.06	2.16
%Carbon	90	98
Specific surface (m^2 g^{-1})	700	250

3. Hybrid composites preparation

Silver flakes and hardener were poured into a first beaker filled with acetone. The solution was sonicated for 5 min. The dispersion of CNTs was assisted by palmitic acid as dispersant agent with a ratio 1:1 by weight. CNTs/ palmitic acid/ epoxy resin suspension was poured into a second beaker filled with acetone. The solution was sonicated for 5 min. After sonication, acetone was evaporated in each beaker. Both beakers were then placed into a vacuum oven at 100 °C for 5 min for degassing. The filled resin and hardener were then poured in a mortar and mixed for 5 min until having a homogenous composite mixture. This mixture was then poured into suitable Teflon molds and cured at 140 °C for 3 h and then at 170 °C for 3 h.

Two types of hybrid fillers have been investigated: DWCNTs/μAg and MWCNTs/μAg. CNT loadings were 0.4 or 1 vol% while silver flake loading ranged from 5 to 24 vol%. Silver flake filled composites were taken as reference materials for electrical and mechanical properties of hybrid composite.

The quality of dispersion of CNTs in epoxy matrix and μAg filled epoxy composites was checked by using FESEM on cryo-fractured surface area.

Electrical conductivity was measured at room temperature using a Novocontrol broadband dielectric spectrometer with two probes method. The samples were tested with voltage amplitude of 1 V in the frequency range [10–2–106 Hz]. The value of conductivity was calculated from the complex impedance Z^* according to $\sigma^*(\omega) = [t/Z^*(\omega)S]$, where t and S are the sample thickness and surface area respectively. The dc conductivity σ_{dc} was taken as the independent frequency part of the real part of σ^* at 10^{-2} Hz. The dynamic mechanical measurements were performed using a Rheometrics ARES Scientific strain-controlled rheometer in the torsion rectangular geometry. The test samples were 1 mm thick, 10 mm wide and 40 mm long. The applied strain of 0.1% was below the limit for linear viscoelastic responses. The temperature dependence of the elastic modulus G' (or storage modulus) in phase with the applied deformation was measured between −150 and 150 °C at 3 °C min^{-1} at a fixed angular frequency of 1 s^{-1}.

4. Results and discussion

SEM images of hybrid composites filled with DWCNTs and MWCNTs are reported in Figs. 3 and 4 respectively. The dispersion of DWCNTs in the hybrid composite leads to the formation of micron-size (1–2 μm) agglomerates of very long CNT bundles. In contrast, MWCNTs are more individualized and well dispersed between silver flakes. As reported in Table 1, DWCNTs have very high surface specific areas (almost three times higher than MWCNTs). The associated intermolecular Van der Waals forces between DWCNTs lead to their arrangement in bundles and bundle agglomerates. The presented dispersion process using sonication, dispersing agent and mechanical mixing is not efficient enough to obtain a homogenous dispersion of DWCNTs in epoxy network.

The dc electrical conductivity σ_{dc} of 0.4 and 1 vol% CNTs filled μAg/epoxy composites is plotted as the function of the silver flake volume fraction in Fig. 5. At low μAg flakes loading, the electrical conductivity decreases slowly with increasing Ag volume fraction at 0.4% vol of DWCNTs or MWCNTs. In this case, the high intrinsic electrical conductivity of Ag flakes does not contribute to the electrical conductivity of the hybrid composite. Increasing MWCNTs content up to 1 vol%, the electrical conductivity increases slowly with increasing μAg vol%.

Above 15 and 17.5 vol%, i.e., the hybrid electrical percolation threshold of respectively MWCNT/μAg and DWCNT/μAg hybrid composites, σ_{dc} is increased by three and one orders of magnitude respectively. Note that the hybrid percolation threshold in MWCNT/μAg hybrid composites is independent of the MWCNTs content. Above the hybrid percolation threshold, MWCNT/μAg hybrid composites are more conductive than DWCNT/μAg hybrid composites. At 25 vol% of μAg, the electrical conductivity of the MWCNT filled hybrid composite is three orders of magnitude higher than that of the DWCNT filled hybrid composite. This hybrid composite is also more conductive than the μAg/epoxy composite indicating a synergistic effect between MWCNTs and μAg inside

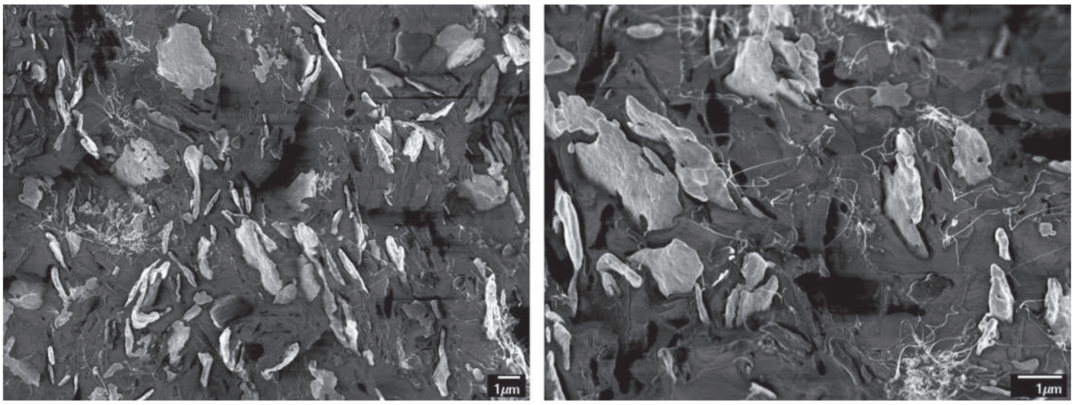

Fig. 3. SEM images of cryo-fractured surface area of 0.4 vol% DWCNTs/20 vol% Ag hybrid composite.

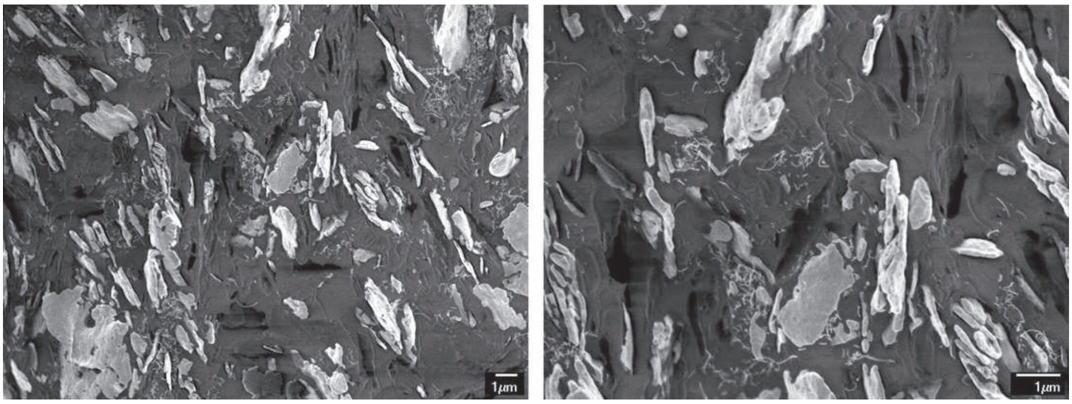

Fig. 4. SEM images of cryo-fractured surface area of 0.4 vol% MWCNTs/20 vol% Ag hybrid composite.

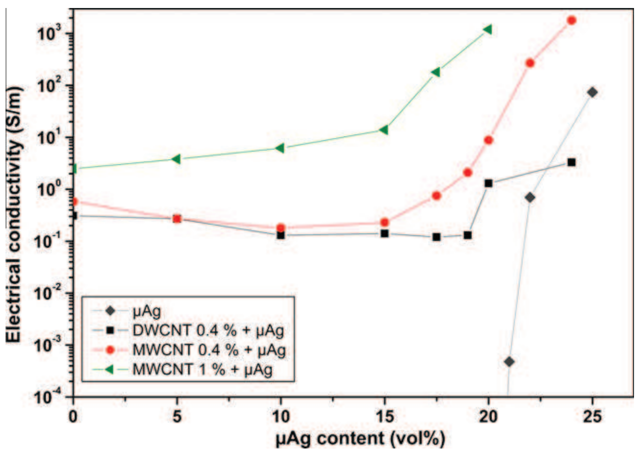

Fig. 5. Dependence of the dc electrical conductivity on the Ag flakes volume fraction for hybrid composites. Data points are connected to guide the eye.

the epoxy matrix. These results are consistent with the analysis of SEM (see Figs. 3 and 4) where micrometer-size DWCNTs agglomerates were observed in DWCNT/μAg hybrid composites in contrast to the shorter MWCNTs well dispersed in MWCNT/μAg hybrid composites. TEM analysis has also shown that MWCNTs are more individualized and shorter than DWCNTs which are organized in large bundles. The improvement of electrical conductivity in the MWCNT/μAg hybrid composites can be associated with the presence of individualized MWCNTs in epoxy matrix forming conductive bridges between μAg flakes as seen in the SEM images of Fig. 4. This morphology explains that the percolating hybrid conductive network is formed at lower silver content than composites filled only with silver flakes. As previously mentioned, the electrical percolation occurs at lower μAg volume fraction in MWCNTs/μAg hybrid composites than in DWCNTs/μAg hybrid composites. This difference is explained by the efficiency of the CNTs dispersion in epoxy matrix: shorter CNTs as MWCNTs are easier to disperse and for a fixed volume fraction, the number of nanotubes in a DWCNTs suspension is higher than the one in MWCNTs suspension.

Similar synergistic effect between silver particles and CNTs have been reported [17,18] in epoxy and polypropylene matrix respectively. Combining micro and nanometric silver is also a way to propose new hybrid filler. Ye et al. [19] showed no improvement of the electrical conductivity in this type of hybrid composite. Contrarily Chen et al. [20] showed a slight increase of the electrical conductivity resulting from better hybrid filler dispersion in polymer matrix. Compared to μAg/MWCNT, μAg/nAg has a lower potential as hybrid filler because of nanopowder aspect ratio near unity, leading to very high percolation thresholds [21].

Percolation threshold, as low as 0.03 vol%, was also obtained with high structure carbon black dispersed in PEI resin [22]. The very long chains of nanosized spherical carbon black particles, kept together by Van der Waals forces and characteristics of high structure carbon black, lead to very low percolation thresholds. According to the Balberg model, a high aspect ratio leads to low percolation threshold. However agglomerates of spherical carbon black particles are less conductive than CNTs because of the great interfacial resistances between each sphere. This behavior was confirmed experimentally by Adohi et al. [23] where CNTs filled polymer composite exhibit, above the percolation threshold, higher electrical conductivity than carbon black polymer composite.

Fig. 6 shows the temperature dependence of the storage mechanical modulus G′ of the DWCNTs/μAg hybrid composites. The drastic drop of G′ is the mechanical manifestation of the glass transition T_g. At a fixed DWCNTs loading of 0.4 vol%, the increase of hybrid composite glass transition temperature T_g with increasing silver flakes content could be explained by increased silver microparticle agglomeration [24]. In the vitreous state, the storage modulus increases with increasing μAg volume fraction. We note that this increase is moderate above 10 vol% of μAg. It is clear that a mechanical reinforcement effect of μAg is observed in hybrid composites and attributed to the restriction of the epoxy chain mobility as other fillers [25]. It is well known in polymer network that the mechanical modulus of the rubber plateau is generally related to the crosslinking density of the materials [24]. In the rubbery state ($T > T_g$), the storage modulus of hybrid composites steadily increases with increasing μAg volume fraction. This increase, attributed to the reinforcement effect of DWCNTs and μAg on the epoxy matrix, is more important in the rubbery state that in the vitreous state. G′ for 0.4 vol% DWCNTs/20 vol% μAg at $T > T_g$ is clearly higher than that of neat epoxy, indicative of the higher crosslink density. In Fig. 7, the temperature dependence of the storage modulus of DWCNTs/μAg hybrid composites is compared to the MWCNTs/μAg hybrid composites and CNTs or μAg filled epoxy composites.

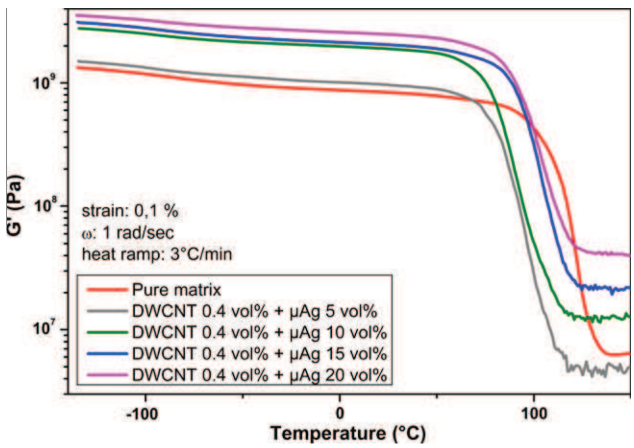

Fig. 6. Mechanical storage modulus of the hybrid composites filled with 0.4 vol% of DWCNTs and 5, 10, 15 and 20 vol% of silver flakes as a function of temperature.

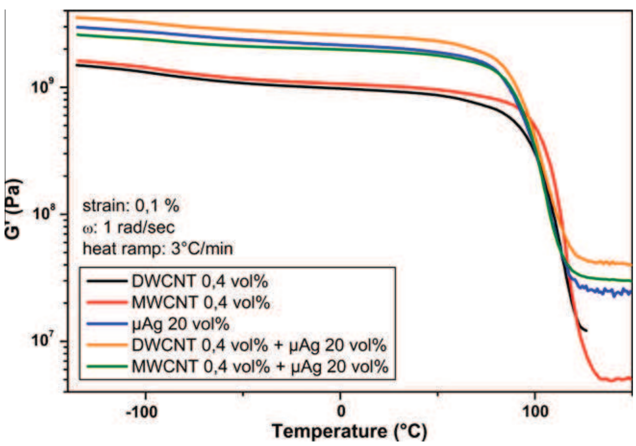

Fig. 7. Mechanical storage modulus of the hybrid composites and CNTs or silver flakes filled epoxy composites as the function of temperature.

In the glassy state, the hybrid composites have a mechanical modulus higher than CNTs filled epoxy composites and similar to the μAg flakes filled epoxy composites. It is well know that CNTs filler improve strength, stiffness and fracture toughness of the polymer matrix [26]. In the rubbery state, the hybrid composites have a storage modulus higher than CNTs or μAg filled epoxy composites. We observe also that the rubbery modulus of DWCNTs/μAg hybrid composite is clearly higher than that of the MWCNTs/μAg hybrid composite. This result is consistent with the rubbery storage modulus behavior in DWCNTs and MWCNTs/epoxy composites. Taking account of the morphology of composites, the tendency of clustering of DWCNTs bundles into agglomerates in hybrid composites results in an increase of the storage modulus at $T > T_g$. The MWCNTs filled μAg composites reveals lower rubbery modulus because of smaller nanotubes agglomerates, shorter MWCNTs and a better dispersion in epoxy matrix.

5. Summary

We have developed a method to disperse CNTs and micrometric silver flakes in a fluid epoxy resin and elaborate hybrid conductive composites. At high volume fraction of silver flakes, a synergistic effect between MWCNTs and silver flakes was found on the dc electrical conductivity. DWCNTs are more difficult to disperse therefore no beneficial impact in electrical conductivity has been observed in hybrid DWCNT/μAg composites. Hybrid composites display also higher mechanical modulus than CNTs or silver filled epoxy composites. Dispersed DWCNTs and MWCNTs act in epoxy matrix as efficient filler improving the storage modulus at vitreous and rubbery state. The highest value of rubbery storage modulus in hybrid composites is characteristics of the tendency of DWCNTs to agglomerate in the epoxy matrix as confirmed SEM investigations.

The first approach of electrical and mechanical properties of CNTs/μAg hybrid epoxy composites shows their potential as conductive adhesives and as reinforcement of the mechanical properties of the epoxy matrix. Future work will be conducted to investigate the thermal conductivity of these hybrid adhesives, their adhesive performance and behavior under thermal ageing.

Acknowledgments

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