Publication information

Title	Highly conductive die attach adhesive from percolation control and its applications in light-emitting device thermal management
Author(s)	Zhang, Xinfeng; Zhang, Kai; Zhang, Min; Yang, Chen; Sun, Hongye; Gao, Zhaoli; Yuen, Matthew M. F.; Yang, Shihe
Source	Applied physics letters , v. 102, (1), January 2013, article number 014101
Version	Published version
DOI	http://dx.doi.org/10.1063/1.4772800
Publisher	American Institute of Physics (AIP) Publishing

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Citation: *Appl. Phys. Lett.* **102**, 014101 (2013); doi: 10.1063/1.4772800

View online: <http://dx.doi.org/10.1063/1.4772800>

View Table of Contents: <http://aip.scitation.org/toc/apl/102/1>

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Highly conductive die attach adhesive from percolation control and its applications in light-emitting device thermal management

Xinfeng Zhang,^{1,a)} Kai Zhang,¹ Min Zhang,¹ Chen Yang,¹ Hongye Sun,¹ Zhaoli Gao,¹ Matthew M. F. Yuen,^{1,a)} and Shihe Yang^{2,a)}

¹Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

²Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

(Received 22 August 2012; accepted 5 December 2012; published online 4 January 2013)

Herein, we reported on the study of percolation dynamics in thermoset-based die attach (DA) materials and its effect on percolation conductivity. Two types of percolation mechanism in thermoset based DA were discovered, i.e., the curing reaction-induced percolation and the physical aging-induced percolation. The former features in a fast percolation network growth rate, which is one order of magnitude higher than the latter. It is demonstrated that the percolation kinetics largely affects the apparent percolation conductivity under the traditional packaging conditions; and reaction-induced percolation allows ultrahigh efficiency in reaching the volume fraction-limiting percolation conductance, resulting in enhanced thermal performance of DA. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4772800>]

Light-emitting diodes (LEDs) have become an emerging and promising candidate for light sources.^{1,2} Unlike conventional incandescent or fluorescent light sources, LEDs directly transfer electricity into light. Therefore, it has many advantages such as high energy conversion efficiency, long lifetime, and small footprint. The internal quantum efficiency of the current inorganic (III–V) semiconductor LED has reached 90%. However, due to the limitations of light extraction, i.e., photons trapped inside the device due to total internal reflection at semiconductor and air interface, most of the trapped photons are converted into thermal energy which substantially increase the junction temperature.³ The increased temperature in LED would greatly decrease the optical performance as well as the lifetime, e.g., the luminous flux decreases by about 5% as the junction temperature jumps by 10°C, and lifetime decays exponentially with the junction temperature. Thus, thermal management in LED is a crucial area of research, and many LED cooling schemes have been proposed.^{4–6}

Die attach (DA) materials, which directly bind the LED die with board, play an important role in the heat dissipation in LED package.^{7,8} The limiting heat dissipation area of DA results in relatively high thermal resistance at the joint, which becomes the bottleneck in heat dissipation in LED packaging. DA with high thermal conductivity has to be adopted to decrease the thermal resistance. Conventional DA uses polymers as matrix with large loading of high thermally conductive fillers, e.g., silver, alumina, silicon carbide to increase the thermal conductivity. However, the thermal conductivity of polymer-based DA is typically around 1–5 W/m·K, limited by the thermal contact resistance of conductive fillers. Different kinds of filler engineering have been developed to increase the effective thermal conductivity of DA.^{9–12}

The apparent thermal conductivity of a particle-filled polymer composite is well-known to be dependent on filler

percolation network formation.^{13,14} Although the percolation behaviors of filler-laden polymer composites have been well described by percolation theory,^{15,16} it is worth noting that most of the theories have examined the percolation phenomenon at a state of thermodynamic equilibration, which is seldom met under the standard industrial packaging conditions. Thus as a practical matter, the achieved apparent percolation conductance always shows large deviation from theoretical predictions. It is of vital importance to get a deeper understanding of the percolation mechanism of particle-laden polymer systems in order to develop strategies to enhance the percolation efficiency. In this work, we focused on the study of percolation dynamics in thermoset-based DA. We demonstrated that there are two types of percolation modes from percolation dynamics analysis, i.e., reaction-controlled percolation and physical aging-controlled percolation. The former features in high percolation rate, which is at least one order of magnitude higher than that of latter. We showed that the conductive percolation efficiency of the silver-epoxy based DA was well-controlled by the percolation dynamics and the reaction-induced percolation is beneficial to enhance the apparent thermal conductivity of DA and improve the thermal performance.

Our model system was composed by conventional silver-epoxy thermosetting composite, which has been widely used in formulating of conductive adhesives.^{9,13} The silver-epoxy composites with and without iodine-treatment were involved in the percolation mechanism study, because it is reported recently the percolation conductance of silver-epoxy composite was greatly increased through iodination of silver fillers.¹³ Prior to the percolation mechanism study, the thermal conductivity of the DA with and without iodine treatment under the standard curing conditions was tested with the standard laser flash method. As shown in Fig. 1(a), the thermal conductivity of non-treated DA (NT-DA) sample with 75 wt. % Ag flake is only 0.9 W/m K. It is greatly increased to 1.2, 1.9, and 2.5 W/m K with silver fillers treated with 0.02 wt. %, 0.05 wt. %, and 0.1 wt. % iodine, respectively.

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: chxzhang@ust.hk, meymf@ust.hk, and chsyang@ust.hk.

FIG. 1. (a) Thermal conductivity of DA with 75 wt. % Ag flakes treated by different amounts of iodine; (b) plots of thermal conductivity with electrical conductivity of IT-DA.

0.1 wt. %, and 0.2 wt. % of iodine, respectively. Further increasing the iodine content to 0.5 wt. % resulted in slightly decrease of thermal conductivity to 2.0 W/m·K. Those values are well consistent with previous study¹³ that there is an optimized iodine content (of around 0.2 wt. %) to achieve the best conductivity. The best result with iodine treatment is to increase the thermal conductivity by 300%.

Fig. 1(b) plots the thermal conductivity with electrical conductivity of the DA with iodine treatment (IT-DA). It is found that thermal conductivity increases with electrical conductivity, almost linearly at least in the regime we studied. This indicates that both of the thermal conductance and electrical conductance enhancements in IT-DA are strongly dependent on the filler percolative network.

The great enhancement of percolation conductance achieved from iodine treatment motivates us to further study the enhancing mechanism. In the thermosetting polymer based composite such as the silver-epoxy, there are many factors affecting the percolation of conductive fillers, e.g., viscosity and rheology variation during curing, curing-induced shrinkage, physical aging, etc. In order to reveal the percolation conductance enhancing mechanism of IT-DA, the dynamic percolation analysis was performed. Fig. 2 shows the dynamic

FIG. 2. Dynamics of electrical resistivity evolution during isothermal curing of both IT-DA and NT-DA under different temperatures.

percolation curves of IT- and NT-DA, from which several distinct features of the percolation curves could be reached:

1. The IT-DA and NT-DA have different types of percolation curves. IT-DA has a simple exponential decrease of resistance at the very beginning of the isothermal curing (10¹ s), and reaches rapidly down to the equilibrium value. However, the percolation curves for NT-DA are relatively complicated, featuring with a two-step growth mode: the first step occurs in the early curing stage and the percolation conductance grew slightly (only by 10² times); the major percolation conductance grew at the following second step, where the percolation conductance typically increased by 10⁴–10⁵ times.
2. The percolation curves maintain the same shape but shift with temperature, indicating that both of the two percolation mechanisms are thermodynamic controlled process. The difference in percolation curve reflects the different physicochemical factors governing the percolation behaviors in those thermosetting systems.
3. It is clearly seen that although higher curing temperature shortens the onset time, the convergent percolation conductance was almost the same. It indicates that different percolation modes result in the delay of percolation; however, they may not change the volume-fraction limited (or self-limited) percolation conductance.

Those results clearly illustrate the existence of two kinds of percolation mechanisms in the formation of percolation network in particle-laden thermoset system. Table I collects the percolation onset time of individual growth step in IT-DA and NT-DA. The conductive percolation onset time for the first step is typically around 10–20 s in both cases, which is most likely an epoxy curing reaction dependent percolation process. In order to reveal the curing effects on conductive percolation, differential scanning calorimetry (DSC) of the DAs was tested. The degree of cure (DOC) was determined by the isothermal DSC results, and plotted with the conductive percolation curves, as given in Fig. 3.

Despite the great difference in percolation curves, the DOC curves between IT-DA and NT-DA showed only slight difference, both of which reached to around 1 within a few

TABLE I. Percolation onset time (t_p) of IT-DA and NT-DA under isothermal curing.

Curing temperature (K)	t_p^1 of IT-DA (s) ^a	t_p^1 of NT-DA (s)	t_p^2 of NT-DA (s)
423	15	15	720
448	10	10	293
463	...	...	93

^a t_p^n stands for the percolation onset time at the different percolation step n .

minutes, suggesting that iodine-treatment did not change dramatically the chemical reaction rate. The percolation curves of the first step in both IT-DA and NT-DA grew along with the DOC curve, supporting the above assumption that it was chemical reaction controlled process.

The discrepancy in percolation dynamics between IT-DA and NT-DA appears after curing reaction was finished: the percolation conductance of IT-DA reaches an equilibrium value, while the conductance of NT-DA continues to grow in the second step which lasts to 10^3 s. The extreme slow growth speed during the second step of NT-DA is reminiscence of many other thermoplastics based conductive polymer composite, e.g., carbon-black filled poly(methyl methacrylate),¹⁴ carbon-black filled polyethylene-based composite,¹⁵ carbon tube filled poly(vinylidene fluoride) (PVDF),¹⁶ etc; which are all related to the polymer matrix relaxation during the physical aging. Although the physical mechanism controlling the

percolation is different during the thermal aging process, they are all featured in a high activation energy and long percolation time. The percolation network is likely to be improved during the physical aging, either due to configurational or positional changes of the cross-linked polymer matrix, or the removal of interfacial polymer layer intercalating between the fillers.

In order to identify more clearly the aging process of epoxy-based thermosets that affects the filler percolation, an Arrhenius plot of the shift factor (t_p) of dynamic percolation curves for non-treated DA was used to determine activation energy of the physical aging process, according to equation:^{14–16}

$$\ln(1/t_p) = \ln A - E_a/RT, \quad (1)$$

where E_a is the activation energy, R is the gas constant, and T is the absolute temperature. The fitted value of E_a is 96 kJ/mol. This value is quite similar to the previously reported activation energy of physical aging of epoxy resin.^{17,18}

So from the percolation dynamic analysis, we can conclude that there are two types of percolation mechanism in thermoset-based conductive composite: the conductive percolation network in IT-DA forms along with the curing of polymer matrix which allows the conductance reaches to the self-limiting value very fast; while the growth of conductive percolation network in NT-DA was mainly dependent on the physical aging of the polymer matrix. It is seen from Fig. 2 that the percolation conductance growth rate of IT-DA is almost 2 orders faster than of NT-DA. So in the traditional NT-DA, a self-limiting conductance could only be achieved at higher temperature or long curing time. The thermal conductivity shown in Fig. 1 should be an apparent percolation conductance; and the observed enhancement of apparent thermal conductivity was obviously caused by the difference in percolation dynamics. Although the exact role of iodine played in the conductive percolation dynamics is still unknown, the current result directly point out the differences in the resulting polymer matrix: the iodine-treated epoxy matrix is seemingly in a “stress” free state; while the non-treated matrix is in a “stress state” and needs an additional “stress” release process to reach the relaxation state. The physical and molecular-level origins of those discrepancies in conductive percolation dynamics due to iodine treatment is under further extensive investigation.

The physical aging-controlled dynamic percolation in thermoset-based composite is the reminiscence of the dynamic percolation in thermomelt-based conductive composite as reported previously.^{19–22} It is recognized that the mechanism of the dynamic percolation process in highly oriented conductive network relies on the relaxation and reorganization of conductive networks and bridging of local contacts, which were initiated through the disorientation and melting of highly oriented polymer crystals.²² The dynamic percolation in thermomelt-based system has been modeled by classical percolation model modified by a second-order particle aggregation process.^{19–22} Considering the similarity between the percolation dynamic curves in thermoset-based system in our study and those of thermomelt-based system, it is reasonable to use the similar model to describe the reaggregation process of thermoset-based conductive composite.^{19–22} This model

FIG. 3. Degree of cure and percolation conductivity dynamics during isothermal curing (a) IT-DA and (b) NT-DA.

combines two approaches: (1) a model for time-dependent cluster aggregation and (2) the classical percolation theory for insulative/conductive systems.^{19–22} Classical percolation theory is well accepted for describing the conduction properties of conductive composites. It gives the following expression for the DC-conductivity above the percolation threshold p_C as a function of filler concentration¹⁹

$$\sigma_{DC} = \sigma_0 \left(\frac{p_A - p_C}{1 - p_C} \right)^\mu, \quad (2)$$

where $\mu = 2$ is usually taken for 3D systems, σ_0 is the conductivity of agglomerates formed by fillers, and p_A is the filler volume concentration.

During the curing, the rearrangement of filler aggregates results in the rebuilt of continuous pathways responsible for the DC percolation. In this case, the p_A should be substituted by a time-dependent effective volume fraction of interconnected filler aggregates. To model the aggregation process of clusters, a second order kinetics process was used.^{19–22} The solution of the kinetic equation gives a time-dependent volume concentration of growing aggregates

$$p_A(t) = p_{A0} + (p_{A\infty} - p_{A0}) \left(1 - \frac{1}{1 + 4kt(p_{A\infty} - p_{A0})} \right), \quad (3)$$

where p_{A0} and $p_{A\infty}$ are the values of initial and final ($t \rightarrow \infty$) volume concentration of the agglomerates, k is the reaction rate, and t is the reaction time. The parameter $p_A(t)$ is the time-dependent volume concentration of conductive filler particles “A” contributing to the conductive network.

The percolation curves shown in Fig. 2 were fitted by combining the formula (2) and (3). The fitted parameters for the percolation curves are listed in Table II, where parameters from IT-DA (the first stage) and NT-DA (the second stage) composites are presented. It is obvious to note that the values of k (which represents the reaction rate of the conductive network formation) in IT-DA samples are almost of 1 order of magnitude higher than those in NT-DA sample, which aligns well with the observation that the IT-DA percolation is much faster than the NT-DA percolation as shown in Table I.

The model clearly reveals the great difference in percolation rates between the chemical reaction-governed and physical aging-governed percolation mode. Our finding disputes the understanding that curing rate was the dominating factor in governing the percolation conductance of composites. Although curing and thermal treatment is believed to be crucial in electrically conductive performance of conductive adhesives, those effects were poorly understood and still in great controversy. Prior conduction studies²³ have shown that the metallic contacts between silver flakes are primarily established during cure. Lu *et al.*^{24,25} found that cure shrinkage, which brings the silver flake particles closer, was the prerequisite. While Inoue *et al.*^{26,27} reported that thermal history has significant effect on electrical conductivity, and the electrical resistivity tends to decrease with increasing curing temperature, even if the samples exhibit full conversion. The current research provides a generic model which clearly illustrates that cure-induced percolation is crucial only in the case of reaction-dependent percolation mechanism, while

TABLE II. Fitting parameters for the modified percolation model.

Composite	p_{A0} (vol. %)	$p_{A\infty}$ (vol. %)	k (s ⁻¹)	σ_0 (S/cm)	p_C (vol. %)	μ
IT-DA, 423 K	5	44	0.024	36 633	26	2.0
IT-DA, 448 K	5	51	0.074	22 538	34	2.1
NT-DA, 463 K	5	42	0.004	36 321	42	2.1

thermal effect is dominated in the physical aging-dependent percolation.

The higher apparent thermal conductivity obtained from the reaction controlled percolation will be beneficial to improve the thermal performance in the LED cooling management. As a demonstration, the IT-DA were applied in LED packaging, acting as both DA (between LED chip and heat slug) and thermal interface materials (between heat slug and printed circuit board (PCB)), as shown in Fig. 4(a). The thermal resistance of LED packages using IT-DA and NT-DA is shown in Fig. 4(b). It is clearly shown that the thermal resistance with IT-DA (7.93 K/W) is much lower than that of LED package with NT-DA (9.08 K/W). The difference is 1.15 K/W, indicating a decrease of total thermal resistance of about 15% by using IT-DA.

In summary, we performed dynamic percolation analysis to study the percolation behaviors of thermoset-based DA. Two kinds of conductive percolation growth modes were identified in the particle-laden thermosets-based polymer matrix system, i.e., reaction-controlled percolation and physical aging-controlled percolation. The percolation network growth rate of the reaction-controlled percolation is 0.024 s^{-1}

FIG. 4. (a) Schematic of the LED packages and (b) cumulative structure function of a LED device packaged with IT-DA and NT-DA.

(curing at 423 K) and 0.074 s^{-1} (curing at 448 K), which is at least one order of magnitude higher than that of latter (0.004 s^{-1} at 463 K) as determined by a dynamic percolation model. It is illustrated that the reaction-controlled percolation growth mode, due to its ultrahigh efficiency in reaching the volume fraction-limiting percolation conductance, is crucial to the enhancement of the apparent percolation conductivity (both thermally and electrically) and the thermal performance of the DA under the conventional packaging conditions. As a demonstration, the DA with high percolation efficiency decreases the total thermal resistance of the whole modules by 15% in a 1 W LED package.

This work was supported by HK-RGC (621810).

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