Microwave heating of metal-filled electrically conductive adhesive curing

Tiebing Wang, Y. Fu†, Matthias Becker‡, Mi Zhou, Johan Liu

Division of Electronics Production, Department of Production Engineering, School of Mechanical and Vehicular Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden

†*Physical Electronics and Photonics, Microtechnology Center at Chalmers, Gothenburg University and Chalmers University of Technology, 412 96 Gothenburg, Sweden*

‡*MACROTRON Process Technologies GmbH, D-85551 Kirchheim bei Munich, Germany*

Abstract

Microwave (MW) as a heating source to cure polymer and polymer-based composites significantly speeds up the curing process. Electrically conductive adhesive (ECA) however normally excludes the use of MW because metal particles because of the possible arcing effect when metal particles are exposed to MW. A new technique named Variable Frequency Microwave (VFMW) has been recently developed, with which the arcing effect is avoided, thus providing us with a rapid process for curing ECA. In this paper, several adhesive samples were cured with VFMW. By analyzing, both experimentally and theoretically, the resulting heating rate as a function of the polymer material, the percentage of the metal particles in the ECAs, the effect of geometric size and shape of the metal particles, as well as the physical parameters of the VFMW, we have demonstrated the applicability of the VFMW technology in curing the electrically conductive adhesives.

Keywords: electrically conductive adhesive, variable frequency microwave, heating rate, power absorption, heat conduction

I. INTRODUCTION

Microwave (MW) as heating source for curing polymer and polymer-based composites has been of great interest for many years. The curing mechanism can be easily understood that the alternating electric field of MW causes a re-orientation of the long-chain molecules of polymers, wherein the friction among molecules takes place to convert the MW energy into thermal heat [1–3]. Because MW heats up the sample at the molecule level, numerous advantages for the use of MW over the conventional thermal treatment are expected [4–8]. For example, a higher heating rate and a more uniform temperature distribution can be easily obtained because all molecules are heated simultaneously without the requirement of thermal conduction. Therefore, MW as an alternative choice as compared with the conventional thermal treatment has been receiving an increasing attention from both the academic and the industrial field.

Electrically conductive adhesive (ECA), as one of the polymer-based composite materials, has been widely used in the electronic packaging industry as a connection medium for mechanical, thermal as well as electrical purposes. Typically it consists of a polymer matrix dispersed with conducting metal particles (normally silver particles). Traditionally, ECA is cured by thermal heat, which is often a rather time-consuming process. Microwaves on the other hand can cause the trouble of arcing due to the exposure of metal particles to microwave.

To solve this problem, a new technique named "Variable Frequency Microwave" (VFMW) has been recently developed [9]. This technique utilizes the microwaves with rapidly varying frequencies (instead of microwaves at a fixed frequency) to irradiate the materials under processing. For metals, the long time of the standing wave can be avoided in such a way that the arcing effect becomes avoided. Metal materials are therefore allowed to exist in the VFMW environment.

Here we report the application of the VFMW cure to metal-particle-filled electrically conductive adhesives. Several kinds of commercially available ECAs were processed by

VFMW. The experimental heating rates are then studied theoretically by the combination of the MW power absorption by the dielectric medium and the heat transfer. Influence of the existing metal particles (the geometric size as well as the shape of metal particle) on the heating rate is theoretically analyzed by studying the spatial distribution of the oscillating electromagnetic field in the conductive adhesive and inside the metal particle.

II. EXPERIMENTAL SETUPS

A. VFMW equipment

MicroCure 2100 from Lambda Co. Ltd. was used as the VFMW oven. This machine has an adjustable input power from 10 to 2000 Watt, and a frequency sweeping time ranging from 0.1 to 10.0 s. The frequency spans a bandwidth from 5.85 to 7.0 GHz. The temperature of the sample is measured with a built-in infrared system and is automatically recorded every second by the computer. For the current work the sweeping time and frequency range were set to be 1 s and 5.85-7.00 GHz, respectively, for every ECA samples.

B. Heating rate for various kinds of conductive adhesives

The adhesives were supplied by Epoxy Technology Inc., which included the epoxy-based thermosetting adhesives and a thermoplastic adhesive, as tabulated in Table 1. For the experiments, adhesives were firstly stenciled onto the substrate. It was then placed into the VFMW cavity for heating. The sample temperature increases with time, which was automatically measured and recorded by the computer. To ensure accurate temperature measurement, the adhesive samples were stenciled with the same volume and shape. The substrate material was chosen such that it is insensitive to MW radiation as to avoid melting due to over-heat.

C. Metal effect on the heating rate

Metal particles (silver) of different sizes and shapes (listed in Table 2) were used to investigate their effect on the heating rate of the ECAs. Every kind of metal particle, without loading into the adhesive, was VFMW irradiated and the heating rate recorded to evaluate the metal heating effect. Again, the assembly of the silver particles has in the same volume and geometric shape as the ECA sample and the same substrate was used.

To evaluate the effect of loading amount of silver particles on the heating rate, spherical particles having a geometric size of 0.5-1 μm were added into the ECA sample E4110. Original E4110 is contains approximately 75-85 wt% (weight percentage) silver particles. The loading effect was studied by only additionally adding 3, 8, and 12 wt% silver particles. After a thorough mixing, the mixture was stenciled into the substrate for microwave irradiation.

D. VFMW parameters effect on the heating rate

Three principal parameters, VFMW sweeping frequency bandwidth, VFMW sweeping time, and VFMW input power, involved in the VFMW technology were checked to study their corresponding effects on the heating rates of the four ECA samples. The sample preparation and dimension were all the same as described above.

III. RESULTS AND DISCUSSIONS

A. Heating rate for various kinds of adhesives

The four types of ECAs were radiated with 300-W VFMW input power. Sample temperatures increase with the radiation time as shown in Fig. 1. Two major characteristics about the heating rates of these ECAS were clearly observed. The thermoplastic adhesive, K5022-115BE, has the largest heating rate, especially at the early stage of radiation. Among the three epoxy-based thermosetting adhesives, H20E is most sensitive to VFMW radiation and reaches a relatively high temperature. Fig. 1 also shows that the heating rates of the four ECAs gradually decrease following the increase of radiation time. Eventually they approach to a type of saturated heating rate.

Theoretically the energy absorbed by a unit volume at spatial position $\boldsymbol{r}$ in a dielectric medium is given by [10]

$$P(\omega, \boldsymbol{r}) = \frac{1}{2}\omega\, \epsilon''(\omega, \boldsymbol{r}) |\boldsymbol{E}(\omega, \boldsymbol{r})|^2 \tag{1}$$

where $\omega = 2\pi f$, f is the frequency of the incident microwave radiation, $\boldsymbol{E}(\omega, \boldsymbol{r})$ is the microwave electric field strength at $\boldsymbol{r}$.

$$\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)\,, \tag{2}$$

is the complex dielectric constant of the material which is $\boldsymbol{r}$-dependent in a composite material, its imaginary part is related to the conductivity $\sigma(\omega)$ of the material by

$$\epsilon''(\omega) = \frac{\sigma(\omega)}{\omega}\,. \tag{3}$$

In our early work, we have studied the electromagnetic wave distribution in a ECA by solving the Maxwell's equations [11]. Similarly here we first calculate the spatial distribution of the electric field intensity in the medium, then the local power dissipation is easily obtained from Eq. (1). In the present study, the spatial volume of the adhesive sample is about $2 \times 2 \times 0.5$ mm^3, which is negligibly small as compared with microwave cavity. We can neglect the spatial variation of $\boldsymbol{E}$ and therefore $P(\boldsymbol{r})$ can be approximated as uniform in the adhesives.

The transient temperature of the adhesive sample exposed to the microwave radiation is obtained from the heat conduction equation

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + P - R\,, \tag{4}$$

where ρ, c_p and k are material density, specific heat capacity and thermal conductivity, respectively. R represents the radiation emitted from the sample. Again, due to the negligibly small spatial volume of the investigating ECA sample as compared with the microwave cavity, we can neglect the spatial variations of the temperatures inside the adhesive samples. The heat conduction equation is therefore much simplified

$$\rho c_p \frac{\partial T}{\partial t} = P - R\,. \tag{5}$$

which results in a linear relationship between the temperature of the sample and the time when ρ and c_p are constant and R is neglected.

Generally speaking, the dielectric properties of a medium depend on temperature. Within the temperature range of interest, the material density is normally constant, while c_p increases with increasing material's temperature [13]. In addition, radiation emission from the sample increases drastically with the increasing sample's temperature. An ideal example of the radiation emission is naturally a blackbody whose emissive power is given by the Stefan-Boltzmann law [14]

$$R_{\text{blackbody}} = \alpha T^4 \tag{6}$$

where $\alpha = 5.67 \times 10^{-8}$ W/m^2-K^4 is the Stefan-Boltzmann constant and T the absolute temperature of the sample. A nonlinear relationship between the sample temperature and radiation time is therefore generally expected and the heating rate gradually decreases. Eventually the heating rate becomes zero when the temperature reaches to such a value that the emissive power from the sample is equal to the power absorbed by the sample from the microwaves. This explains well the generally characteristics of the heating rates of our ECA samples (see Fig. 1).

In our investigations, f and $|\boldsymbol{E}|$ are kept constant for all samples, and the loading amount of silver particles are also similar for the four ECAs, namely, about 75-85 wt% based on the percolation theory [12]. It can thus be concluded that the difference in the heating rates of the four ECAs is principally determined by the dielectric properties of the adhesive material. By Table 1 and Eq. (3) it is easy to understand why K5022-115BE has the largest heating rate and E4110 the lowest. Fig. 1 reflects the resistivity values listed in Table 1 via Eq. (3) that low resistivity (high conductivity) results in a high power absorption, and therefore a high heating rate.

It is worthwhile to note that a high heating rate does not necessarily indicate a high curing rate. Indeed, of all the thermosetting ECAs investigated, only E4110 obtains its curing strength within 1-min radiating time, even though its heating rate is the lowest among the three samples. Therefore, to employ microwaves for ECA curing cycles, an appropriate curing agent should also be taken into consideration. The combination of a lower cross-linking reaction temperature and a high reaction speed would be a better choice.

B. Metal effect on the heating rate

To study the effect of metal particle loading on the heating rate of ECA, we add to sample E4110, respectively, 3, 8, and 12 wt% silver spherical particles having a size of about 4-7 μm. After a thorough mixing, the ECAs were stenciled onto the substrate and then heated by VFMW at 300-W microwave input power. Measurement spectra of adhesive temperature versus VFMW radiation time are presented in Fig. 2, which indicates that low silver loading is preferable for the microwave energy absorption.

Because the ECA E4110 is supplied in a filled format with silver particles, we first study the heating rates of pure metal particles (rather than in the ECA). The metal particles have different geometric sizes and shapes and are directly radiated by VFMW at input power of 300 W. The results are presented in Figs. 3 and 4 for spherical and flake particles and different sizes. It is demonstrated here that: 1) For spherical fillers, the small particles results in high heating rate; 2) Flake particle size has no evident effect on the heating rate; and, 3) Spherical particles have high heating rate than the flakes of comparable size.

Theoretically, metal particles absorb and convert the microwave energy into thermal heat by the combination of Joule effect and the dielectric loss. Due to metal conductive nature, the dielectric loss is negligibly small. Conduction electric current induced by the external electrical field dominates the thermal effect. In addition, it is well known that alternating electromagnetic fields propagate in the spatial region that is not conductive. And there is a small penetration of the electromagnetic wave into the metal, which is called the skin effect.

The skin depth decreases following the increase of the AC frequency:

$$\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \, . \tag{7}$$

It is easy to show that in the application frequency range of our VFMW (about 6 GHz), δ is about 1.0 μm.

When the geometric size of the metal particle is less than 1.0 μm, the electric field can penetrate through the whole metal particle. Conduction current driven by the electric field is therefore also expected to run through the whole metal particle, resulting in a large local power dissipation due to the Joule effect. When the particle size becomes very large (e.g., the 2-3 and 4-7 μm spherical particles and all sizes of flakes in this work), the microwave radiation penetrates only a small portion of the particle. Since microwave power dissipation happens only in this small spatial region, the heating rate is expected to be small. This explains the measurement results of Figs. 3 and 4 that when the size of metal particles exceeds 1.0 μm, particle size and shape impose no direct effect on the heating rate.

Figs. 3 and 4 show that the highest temperature in the pure silver particle assembly after 1-min radiation time is below 90 ^{o}C. Typically for the 4-7-μm spherical particles, the temperature is around 70 ^{o}C. Fig. 2 shows that additional load of silver particles results in a decreased heating rate. With 8 and 12 wt% additional loads, the heating rate approaches to the heating rate that characterizes the large-size metal particles. It is therefore concluded by comparing Figs. 1-4 that the base polymers of the ECA samples are more effective in absorbing microwave energies than the silver particles.

C. VFMW parameters effect on the heating rate

Three built-in parameters with the VFMW oven were carefully checked for optimizing the heating rate: VFMW frequency sweeping bandwidth, VFMW sweeping time for each cycle, and VFMW input power. It was found that the first two parameters have little effect on the heating rate, whereas the microwave input power significantly affects the heating rate of the processed materials, as illustrated in Fig. 5. Keeping all other parameters unchanged, a high microwave power input, in general, always leads to a high heating rate.

Eq. (1) clearly shows that the microwave power dissipation is proportional to the oscillating frequency of the electric field, which has a bandwidth from 5.85 to 7.00 GHz in our VFMW oven. A weak dependence of the heating rate on the frequency bandwidth is thus expected. VFMW sweeping time for each cycle is expected to have little effect on the heating rate due to the small volume of the ECA. This is a partial support to our early approximation that the $\boldsymbol{E}$ and P are uniform within the spatial region of the ECA due to its small volume and therefore a uniform sample temperature.

Whereas on the other hand, the power dissipation is directly proportional to the VFMW output power (which is proportional to $|\boldsymbol{E}|^2$). Neglecting the emissive power from the ECA we would expect a linear relationship between the VFMW output power and the heating rate. However, experiments of Fig. 5 show a rather strong nonlinear effect. This can be expected by Eq. (6) that the emissive power is proportional to the absolute temperature of the sample, while the temperature units in the figures are ^{o}C.

Theoretically we can re-write the heating rate of the ECA as

$$\rho c_p \frac{\partial T}{\partial t} = \frac{1}{2}\sigma|\boldsymbol{E}|^2 - \beta T^4 \,, \tag{8}$$

where $|\boldsymbol{E}|^2$ is the VFMW input power. Taking the conductivity of E4110 ECA as 1.0, the conductivities of H20E, EE129-4 and K5022-115BE are about 1.25, 1.5 and 2.0-10.0 (see Table 1). β represents the deviation of the emissive power of the ECA from the perfect blackbody, which is generally referred as grey-body. Here we have neglected the heating effects of metal particles. Setting $\rho c_p = 1$, $\beta = 1$, and $T = 0.5$ at $t = 0.0$, Fig. 6 shows the results of the heating rates for different MW input powers and conductivities of the adhesive.

It is easy to see that Fig. 6 in principle explains our experimental results. Further quantitative investigation about the metal particles and the mixture of polymer and metal particles in the ECA format however demands detailed knowledge about the dielectric properties of the adhesives and the spatial distribution of the electric field in the assembly of metal particles and ECAs, which is being exploited at the present research stage.

IV. CONCLUSIONS

In a brief summary we have demonstrated a new technique named "Variable Frequency Microwave" in the application of curing metal-particle-filled electrically conductive adhesives. Following conclusions were derived:

1. VFMW can be used to cure metal-filled electrically conductive adhesives without arcing problem.
2. VFMW has the capacity of heating ECAs rapidly. The heating rate is closely relating to the dielectric properties of the constituent polymer.
3. The speed of the whole curing process depends not only on the heating rate but also on the curing reaction rate that is dominated by both the matrix material as well as the curing agent.
4. Small metal fillers are beneficial than larger particles for improving the heat rate.
5. The effect of metal fillers on the ECAs heating rate differed from one polymer to another which depended on the individual dielectric loss with respect to the Joule effect of the metal particles.
6. Microwave input power is a critical parameter affecting the heating rate, while other physical parameters of the VFMW technology have little effect.

We have qualitatively explained the experimental results by analyzing theoretically the heat absorption conduction processes in the ECAs. Further quantitative investigation however demands detailed knowledge about the dielectric properties of the adhesives and the spatial distribution of the electric field in the ECAs as well as the penetration and reflection of the electromagnetic field in the metal particles (and their dependence on the particle size and shape), which is being exploited at the present research stage.

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TABLES

TABLE I. ECA samples tested by VFMW.

Name	E4110	H20E	EE129-4	K5022-115BE
Recommend cure time	$150^oC/15min$	$175^oC/45s$	$150^oC/15min$	$150^oC/3-5s$
	$100^oC/1h$	$150^oC/5min$		
	$80^oC/3h$, RT/72h	$120^oC/15min$		
Volume resistivity [Ω-cm]	0.0005	0.0004	0.00033	0.0001-0.0005
Die shear strength	10kg/3400psi	10kg/3400psi	10kg/3400psi	1.54kg, 530psi
Degradation temperature	sub-ambient	80^oC	90^oC	unknown
Remark	epoxy thermoset	epoxy thermoset	epoxy thermoset	thermoplastic

TABLE II. Experimentally used silver particles from KEBO Lab.

Stock No	41597	41599	11402	14639	00783	14755
Shape	spherical	spherical	spherical	flake	flake	flake
Size [μm]	0.5-1	2-3	4-7	90%<3	APS [a]<7.5	90%<20

[a] APS: Averaged Particle Size.

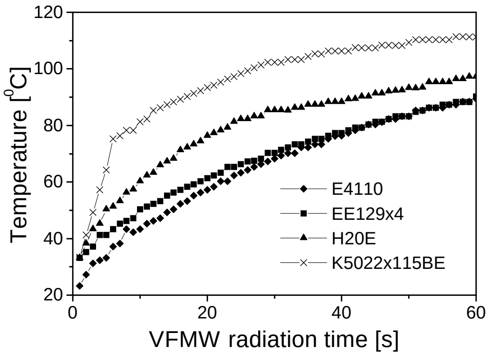

FIG. 1. Heating curves for different ECAs radiated by VFMW (300 W).

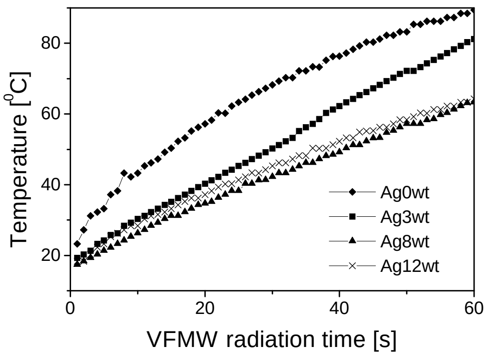

FIG. 2. Heating curves for E4110 with different silver loading fractions radiated by VFMW (300 W).

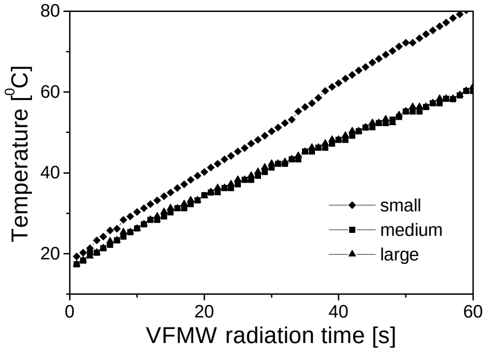

FIG. 3. Heating curves for pure spherical silver particles in different sizes radiated by VFMW (300 W).

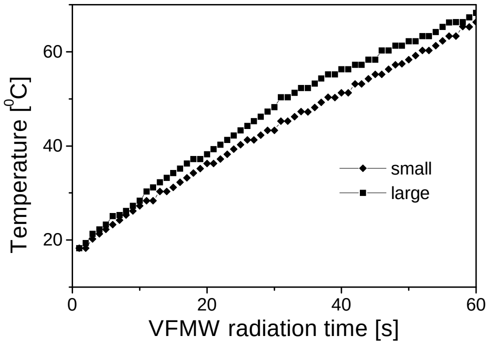

FIG. 4. Heating curves for pure flake silvers in different sizes radiated by VFMW (300 W).

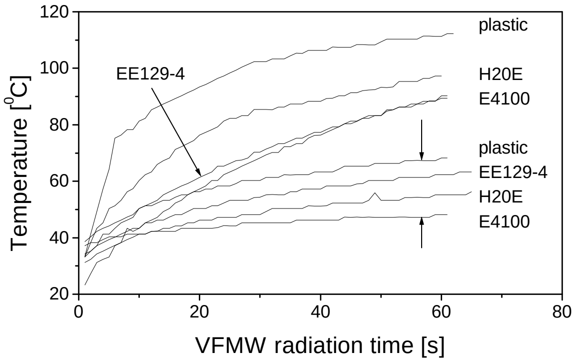

FIG. 5. Heating curves for different ECAs radiated by VFMW at power of 100 W (between two vertical arrows) and 300 W.

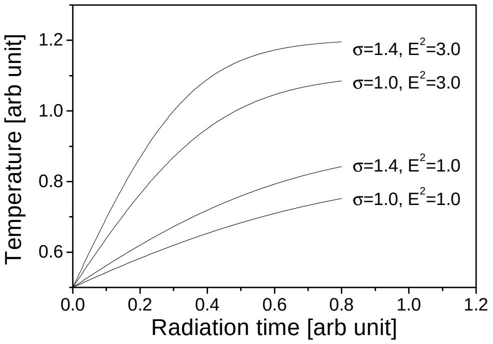

FIG. 6. Theoretical heating rates for different adhesives having different conductivities radiated by different VFMW input powers.