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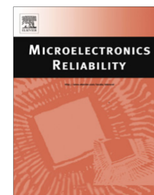

Monitoring extent of curing and thermal–mechanical property study of printed circuit board substrates

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ABSTRACT

Precise control of curing conversion for epoxy-based printed circuit board (PCB) substrates and clarification of curing–property relationship are critical for the performance and reliability assessment, and for the design optimization of electronic systems. In this article, various epoxy composites for PCB substrates were analyzed by infrared spectroscopy (IR), differential scanning calorimetry (DSC), rheometry, dynamic mechanical analysis (DMA), and scanning electron microscope (SEM). Compared with mid-IR and DSC, near-IR (NIR) is found to be a reliable method for the characterization of curing conversion process by detecting the consumption of epoxy groups. And DMA is a powerful method for measuring the conversion of PCB materials by testing glass transition temperatures (T_g) and viscoelastic properties. The curing behaviors of a variety of epoxy composites show distinct differences in both curing rate and activation energy, and the growth tendency of T_g with curing conversion also changed depending on the material compositions. Correlation of curing conversion versus thermal properties shows that the activation energy of curing at different stage by DSC resembles the tendency of T_g transitions tested by DMA. Mechanical properties of the composites show close relationship with the curing conversions. Peel strength, the indicator of adhesion strength between copper foil and epoxy composites, was tested on all the specimens of different curing conversions, and the results showed a maximum value at curing conversion between ca. 90 and 95%.

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1. Introduction

Laminates for printed circuit broads (PCBs) are composite materials, obtained by pressing layers of a resin-impregnated filler material under heat and pressure, the resin in which is mostly epoxy [1]. The curing procedure therefore has great effect on the performance of epoxy composites for PCB substrates, as well as their adhesion with copper foil. And the adhesion strength influences the stability and reliability of electronic systems. With the request of miniaturized designs and higher performance of semiconductor electronic devices, PCB materials are expected to perform even better than ever before [2,3].

Ordinarily, the epoxy composites for PCB substrates are composed of glass fiber, fillers, and a variety of epoxy resins and hardeners, like amines, phenolic resins, or imidazoles, as well as modifiers such as rubbers, thermoplastics and other materials. Consequently, a much more complicated procedure is requested for the characterization and optimization of curing conversion of these materials rather than that of neat resin systems. Therefore, from the view of both theoretical research and industrial applications, to characterize the conversion of epoxy composites precisely after processing, and to establish a relationship between curing conversion, structure, and property for different epoxy composites for PCB substrates become an urgent and tough task.

For neat thermosetting resins without modification or blending, it has been revealed previously in numerous systems that there is a quantitative relationship between the curing conversion of the thermoset and its glass transition temperature (T_g) value, independent of the time–temperature cure history [4–9]. The equation derived by DiBenedetto [10] for predicting the glass transition temperature of a polymer based on the crosslink density of the network was generally used as a starting point.

$$\frac{T_g - T_{gu}}{T_{gu}} = \frac{X_c\left(\frac{E_x}{E_m} - \frac{F_x}{F_m}\right)}{1 - X_c\left(1 - \frac{F_x}{F_m}\right)} \quad (1)$$

In this equation, X_c is the mole fraction of segments that are crosslinked, T_{gu} is the glass transition temperature of the uncrosslinked polymer, E represents the lattice energy, F is the segmental mobility, and the subscripts x and m refer to the fully crosslinked and uncrosslinked polymers respectively.

For most polymers, the mobility of crosslinked units is essentially zero, so Fx/Fm can be set equal to zero [11]. Rearranging Eq. (1), one can obtain:

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$$T_g = KT_{gu}\frac{X_c}{1-X_c} + T_{gu} \quad (2)$$

where K contains the lattice energy terms. A plot of T_g as a function of $X_c/l(1 - X_c)$ should result in a straight line. Although experimental results always have some deviations from theoretical prediction, this can still be useful during application, since T_g is often a simpler and more sensitive measurement than conversion itself.

DSC is always used to characterize the curing conversion of neat epoxy resins by testing the T_g at different stage. However, this method has great limitations when multi exothermic peaks appear during resin curing or several glass transitions evolve in multi-component systems.

As a substitution, Infrared spectroscopy (IR) is also widely applied for curing conversion testing by observing the area change of functional groups relative to that of the internal standard groups [12]. However, in our previous work, it has been found in Mid-IR (MIR) that the bands of epoxy group at 916 and/or 851 cm^{-1} may be overlapping other peaks, which hampers the conversion calculation of epoxy group by MIR method [13].

Whereas, Near-IR (NIR) has been successfully applied in various fields, including curing monitoring [14], resin and volatile-content quality control [15], storage characterization of prepregs, etc. While optical-fiber-connected NIR can also be used for in situ test of various reactions [16,17]. However, no report has been published on the characterization of PCB materials by NIR till now.

Meanwhile, the influence of curing conversion on structure–property relationships is somehow inconsistent and limited in scope for neat epoxy resins. For example:

(1) The maxima of the flexural or tensile modulus and impact resistance appeared well below full conversion and depended on the number-average functionality of the curing system [18].
(2) The tensile modulus decreases whereas the fracture toughness increases with postcuring [19].
(3) The room temperature modulus decreased with increasing extent of conversion [20].
(4) Tensile modulus decreased at the conversion range of 75–90%, while a minimum value was found in the fracture toughness at ~90% conversion [21]. The fracture toughness increased up to nearly full cured [22].

Whereas, considering the complexity of multi-component PCB materials, one can easily anticipate that the functional relationship between T_g and curing conversion cannot be applied into these systems, while the change of property with conversion should also be re-explored for optimization of the PCB performance.

At the present time, it is imperative for the PCB industry that a feasible method can be applied for precisely testing the curing conversion of epoxy composites for processing control, and a curing-property relationship could be established for optimization of PCB performance. In this work, we compared various instruments for the characterization of curing conversion of epoxy composites, and demonstrated that NIR and DMA are powerful instruments for both judgment of curing conversion and viscoelastic analysis of materials at different curing stage. Moreover, the curing behavior, conversion, and thermo-mechanical properties were correlated with each other for PCB materials.

2. Experimental methods and theory

2.1. Materials

The fresh roll of epoxy prepregs from Panasonic (Japan) and Elite Material Co. (Taiwan, China) were used for the study. The prepregs for PCB are generally composed of epoxy/phenolic resin or epoxy/dicyandiamide as specified by the manufactory. We random selected three samples EMC-285 (Elite Material Co.), R-1551v, and R-1570 (Panasonic) as representatives, and herein denote them as *Sample a*, *Sample b*, and *Sample c*.

Two kinds of samples for investigation were prepared by using either epoxy prepregs directly, or resin components of prepregs with glass fiber removed.

2.2. Experimental methods

2.2.1. Infrared spectroscopy monitoring

Mid-infrared (MIR) spectroscopy was performed with a Thermo Nicolet Nexus 440 spectrometer, and near-infrared (NIR) spectroscopy was performed with a Nicolet NEXUS 470 FTIR spectrometer. For the in situ NIR study, fresh prepregs were placed in the compartment and monitored in situ in the near-infrared region (11000–4000 cm^{-1}) at different temperatures.

2.2.2. Rheological test

The melt viscosity variations of resin components without glass-fiber were recorded on an ARES-9A rheometry instrument. All the samples were tested under a parallel plate mode with a controlled strain of 1% and frequency of 1 Hz. The resin components, which were from the fresh prepregs with glass-fiber removed, were sandwiched between the two round fixtures (diameter 25 mm), then the plate distance was adjusted to 1.0 mm quickly at the test temperature. As the standard industry processing temperature of the PCB prepregs is 171 °C, the test temperature was fixed at this value in order to provide the most useful information for researchers in this area.

2.2.3. Dynamic mechanical analyses (DMA)

The dynamic mechanical properties were collected with a Netzsch DMA 242 operating in the tensile mode at multi oscillation frequencies of 1, 2, 5, and 10 Hz. The specimens were prepared in the form of cuboid bars with dimension of 15 × 50 mm^2, the thickness of the sample from one layer of cured epoxy prepregs was measured each time. The data were collected from 0 °C to 260 °C at a scanning rate of 3 °C/min.

2.2.4. Mechanical test

The T-peel adhesion strengths between copper foil and epoxy composites were determined using an Instron Model 5565 universal tester at a constant temperature. Each test reported was the average of at least five sample measurements. Tensile strength of epoxy composites was tested according to China State Standard GB 1040-79, while peel strength was tested according to IPC-650-650 standard.

2.2.5. Scanning electron microscope (SEM)

The structure of samples after peeling test were observed under a SEM (Tescan TS 5163MM). All samples were coated with gold and mounted on copper mounts.

2.2.6. Different scanning calorimetry (DSC)

Calorimetric analyses were carried out on a Mettler DSC-823e thermal analyzer. Samples of approximately 5 mg in weight were cured in aluminium pans in a nitrogen atmosphere. The calorimeter was calibrated using indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration).

In the isothermal and dynamic curing process the degree of conversion by DSC (α_{DSC}) was calculated as follows:

$$\alpha_{DSC} = \frac{\Delta H_t}{\Delta H_{totol}} \quad (3)$$

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