Test Method

Non-destructive DRIFT spectroscopy measurement of the degree of curing of industrial epoxy/silica composite buildup layers

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ABSTRACT

The degree of curing of epoxy composites and coatings is one key parameter to control the reliability of manufacturing processes, particularly in printed circuit board (PCB) manufacturing where epoxy buildup composites are partially cured before processing. We show that the reaction of curing of an industrially relevant buildup composite (epoxy-phenol reinforced with silica fillers) can be monitored by diffuse reflectance infrared Fourier transform (DRIFT) in the near-infrared range. The accuracy of DRIFT measurements is confirmed by comparison with measurements in transmission mode on reference composite samples. DRIFT is demonstrated to offer an easy and reliable measurement of the epoxy degree of curing on PCB coupons.

1. Introduction

Epoxy composites and coatings are thermoset materials widely used in aerospace, construction, and microelectronics [1–3]. In the area of microelectronics packaging, epoxy composites are extensively used as buildup layers for multilayer printed circuit board (PCB) manufacturing, ensuring electrical insulation between wiring copper levels [4,5]. In the context of the miniaturization of electronic devices, the thickness of the buildup layers can decrease down to a few tens of microns, in the form of *prepregs* (epoxy/fibers) or *b-stage* films (epoxy/glass beads) [6]. In general, the films are partially cured ("pre-curing") before processing and fully cured afterwards ("post-curing"). At each step of the process, the degree of curing of the epoxy matrix dictates its thermal, mechanical, dielectric and chemical properties [7]. The control of the curing conditions and kinetics is therefore of primary importance to achieve reliable and repeatable results [8,9].

The basic method to measure the degree of curing of thermoset materials is differential scanning calorimetry (DSC) [10–16]. However, this technique has no molecule-specificity. Moreover, it is destructive and is not suited to thin layers and coatings. On the other hand, other techniques have been used to measure the degree of curing on composite thin layers and coatings, such as dielectrics spectroscopy [17,18], dynamic mechanical analysis [18,19] or ultrasonic probes [20,21]. They offer an indirect and relative measurement of the degree of curing through physical parameters (permittivity, mechanical moduli, speed of sound …), and are thus ill-suited to in depth kinetic analysis.

In contrast, vibrational spectroscopies such as infrared (IR) and Raman are powerful techniques for *in situ*, *operando* analysis. They are increasingly used techniques [22], being rather cheap, easy to perform, non-destructive, non-invasive and in/on-line applicable. They provide a direct, molecule-specific, measurement of the degree of curing by monitoring the spectral signature of the epoxy groups. For example, Escola et al. showed that the measurement of the degree of curing in epoxy paints can be assessed by diffuse reflectance infrared Fourier transform (DRIFT) in the near-infrared range [23]. In the case of epoxy/silica composites near-IR (NIR) is used in order to avoid the overlapping broad band coming from the silica fillers [23–26]. In this letter, we show that DRIFT method in the NIR domain is well appropriated to measure the degree of curing of highly loaded epoxy-silica composite and suited to measurements onto buildup layers in PCB. To our best knowledge, this is the first application of DRIFT method for the evolution of the degree of curing, directly on industrially relevant buildup films.

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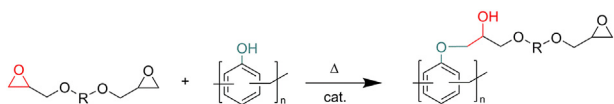 *E-mail address:* jean-louis.bantignies@umontpellier.fr (J.-L. Bantignies).

Fig. 1. Crosslink formation of the epoxy network during the reaction of curing.

2. Materials and methods

2.1. Materials

The epoxy/silica composite material is supplied by Ajinomoto Fine-Techno Co., Inc., as "Ajinomoto buildup films" (ABF) GX-T31R in the form of *b-stage* films with a thickness of 35 μm. The matrix consists of di-epoxy-terminated molecules (mainly bisphenol A, bisphenol F and 1,6-bis(2,3-epoxypropoxy)naphthalene) and phenol-formaldehyde oligomers. The reaction of curing is an etherification, involving the oxirane ring opening by nucleophilic attack of the phenol with the presence of a catalyst (Fig. 1). To prevent unwanted aging, the uncured films are stored in a freezer at $-18\,°C$. The zero degree of curing ($\alpha = 0$) refer to the curing state of the as received films. Silica fillers are mainly used to reduce thermal mismatch between copper and epoxy. Their mean-diameter is 380 ± 120 nm and their amount is 62 ± 1 wt. % (Fig. 2A).

In order to reach an optimal absorbance (about 1.2 in the NIR) in transmission mode and thus enable comparison to the DRIFT signal, *b-stage* reference samples each consisting of a stack of 16 ABF layers were prepared by sequential lamination of ABF layers. The reference samples were partially cured at $180\,°C$ in air with a curing time varying from 0 to 120 min. On the other hand, the industrial coupons consisted of double-sided sandwich composites (Fig. 2B). Copper foils of 20 μm thickness were laminated on both sides of a flame retardant 4 (FR-4) core composite (~ 0.9 mm thick, giving the mechanical strength). After chemical roughening of the copper surface, the ABF layer (35 μm) were laminated on top of the former (2 min, $100\,°C$, 10^5 Pa). The thickness of the whole industrial coupons was about 1 mm.

2.2. Spectroscopic methods

NIR absorption spectroscopy experiments were carried out using a Bruker IFS 66V FTIR spectrometer, equipped with a black body (Globar) source, a KBr beam splitter, and two detectors: one mercury cadmium telluride (MCT) and one deuterated triglycine sulfate (DTGS). For each measurement, three different areas of each sample were probed in order to check the reproducibility of the results (standard deviations below few percent). Spectra were recorded in the range 4000–7000 cm^{-1}, with a resolution of 4 cm^{-1}, as the sum of 64 scans (acquisition time of ca. 1 min).

In transmission configuration, micro-NIR experiments were performed with a Hyperion 2000 microscope (Bruker Inc.) working in confocal configuration using × 15 objectives and coupled to the infrared spectrometer (Fig. 3A). The spectral resolution was 4 cm^{-1} and 64 scans were accumulated for each spectrum.
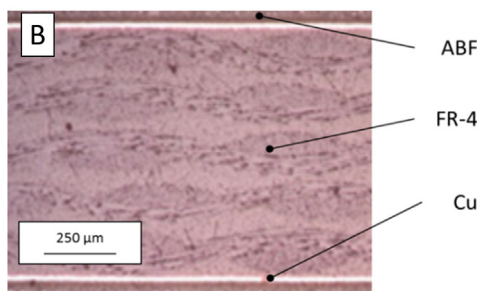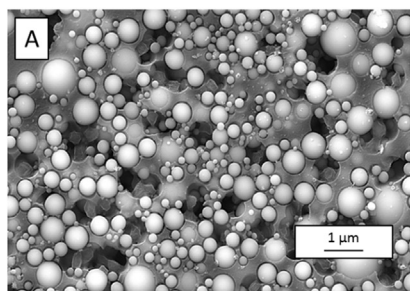
Diffuse reflectance (DRIFT) is based upon the collection of radiation that has been scattered from the sample [27]. DRIFT measurements were performed with the Selector™ Specac accessory placed in the sample compartment of the FTIR spectrometer. A symmetric pair of high-magnification large-aperture confocal ellipsoidal mirrors (Fig. 3B) is the key element of the experimental apparatus. This DRIFT accessory uses optimized off-axis optics configuration which selectively collects and maximizes the diffuse component of the reflected light, whilst minimizing the specular one. The DRIFT signal of the sample is normalized with respect to that a non-absorbing KBr standard, and the corresponding relative diffuse reflectance is called R_∞.

Both transmission and DRIFT measurements were performed *ex situ*: samples were first partially cured at $180\,°C$ for various times, and then analysed at room temperature in any cases.

The Kubelka-Munk (KM) model provides a simple solution for relating the relative diffuse reflectance to the absorbance in the case of an infinitely thick sample: one can show that the function $F(R_\infty)$ defined as:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{1}$$

is proportional to the linear absorption coefficient k of the sample divided by a scattering coefficient s dominated by the particle size and refractive index of the sample. Within the KM theory, s is assumed to be independent of the wavelength [28], so that $F(R_\infty)$ is directly proportional to the absorbance. Thus $F(R_\infty)$ spectra measured in DRIFT configuration are expected to be quite similar to absorbance spectra measured in transmittance configuration.

$$F(R_\infty) = \frac{k}{s} \propto \frac{A}{s} \tag{2}$$

Note that in the KM model the sample must satisfy the assumption of semi-infinite thickness, *i.e.* transmittance of the sample must be close to zero. For polymers, this is typically achieved for thicknesses of a few millimetres [29]. Scattering is much stronger for composites, so that the transmittance of 35 μm b-*stage* reference samples falls down to about 6%. Therefore the transmittance of the superficial ABF layer of the industrial coupons is estimated to be about 90% but the reflectance of the underlying copper layer is close to 100% which makes the samples completely opaque to the NIR signal.

3. Results and discussion

3.1. b-stage reference samples

Epoxy moieties are featured by two infrared-active modes at 915 cm^{-1} (Middle IR, MIR) and 4528 cm^{-1} (NIR), assigned to C-O-C deformation and to the combination of CH (3050 cm^{-1}) and CH_2 deformation (1460 cm^{-1}), respectively [27,28]. For neat epoxy resins, the intensity of the MIR peak is strong enough for a quantitative analysis. However, this is no longer possible for epoxy/silica composites due to the overlap with a broad and intense mode of silica around 1096 cm^{-1}.

Alternatively, we monitored the combination mode in NIR at

Fig. 2. SEM image of b-stage film microstructure (A), and optical microscopy image of an industrial test coupon (B).