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A RAPID TEST FOR EVALUATING THE DEGREE OF CURE IN CFRP COMPOSITES*

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A noncontact optothermal method is described for possible application to routine industrial evaluation of the degree of cure in polymeric composites. The surface of the part is heated by a laser beam or other radiative source while its temperature evolution is continuously monitored with an infrared detector. A strong exothermal peak is observed when the material is partially or totally uncured. Changes in the signal shape related to variations of the part geometry or environmental conditions are minimized by a differential approach comparing subsequent heat cycles on the same area. Results obtained with cured or uncured graphite-epoxy prepreg sheets are presented.

Quality control of composite materials and structures is a very active research field [1, 2]. Graphite-epoxy composites are particularly subject to strict inspection procedures because of their increasing utilization as primary structures in safety-sensitive fields such as in the aircraft industry. The mechanical properties of carbon-fiber-reinforced-plastics (CFRP) structures are much affected by the degree of cure of the resin matrix both before and after processing. Before processing, the slightly precured prepreg sheets which are shipped to the manufacturer in refrigerated cells are normally inspected to verify that the required pre-cure level has not been exceeded [3]. After lay-up and autoclave curing, the degree of polymerization must be sufficiently high to assure the required mechanical performance.

A number of approaches are possible to evaluate the degree of polymer cure, including spectroscopic, calorimetric, mechanical, electromagnetic or ultrasonic methods [1, 4, 5], the most widely used being the spectroscopic and the thermal techniques. Infrared spectroscopy can provide quantitative data concerning the amount of unreacted epoxy groups. For best results measurements must be made in transmission and, in the case of cured composites, this requires destruction (grinding) of the sample. The diffuse reflectance method has the advantage of being noncontact and nondestructive, but is of limited value for quantitative work [4].

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Thermoanalytical methods include differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis and thermogravimetry techniques [1, 3, 6]. The thermoanalytical approach is very powerful but rather time-consuming, requiring careful sample preparation and good thermocouple contact.

In this paper we analyze the possibility of an in-situ optothermal approach by which the composite material is surface-heated to the curing temperature by a laser beam and temperature-monitored by an infrared detector. No thermal flow from the sample to a bonded thermoelectric sensing device is involved, so that the true surface temperature is sensed without any thermal inertia. The thermal history curve for the first heating cycle is compared to subsequent curves obtained under similar conditions to identify at least qualitatively the occurrence of irreversible transformations in the heated volume. The material can thus be inspected rapidly and with minimum sample preparation, while the differential approach makes the measurement relatively insensitive to the part geometry and boundary conditions. Preliminary experimental results obtained with partially cured graphite-epoxy prepregs are described.

Description of the method

Photothermal techniques [7–9] are a rapidly expanding research field for the inspection of industrial materials. The part is surface-heated by a laser or similar radiative source and the temperature evolution is monitored to evaluate the thermal parameters of the material such as the thermal diffusivity. Variations in the thermal parameters related to the curing of epoxy metal adhesive have recently been reported [10] using a photothermal approach to monitor the thermal-wave propagation across the adhesive during room-temperature curing.

Thermal propagation modeling in layered composite media is relatively complex because of the material inhomogeneity and anisotropy as well as three-dimensional spread and surface loss considerations. A considerable simplification is possible however if the relevant signal can be obtained through a differential approach so that common-mode noise can be eliminated. An approach of this kind can be followed to detect bonding defects by space-domain or time-domain thermal-image differentiation [13]. A similar principle is applied in this paper for the evaluation of the extent of curing in a graphite-epoxy sheet.

The experimental apparatus is shown in Figure 1. A laser beam, or an alternative radiative heat source such as a heat lamp, is used to heat the inspected prepreg to the curing temperature, typically in the 200–300° range, during a time period of the order of some tens of seconds. Although such a temperature level is substantially higher than the recommended autoclave-curing temperature, it is sufficiently low to

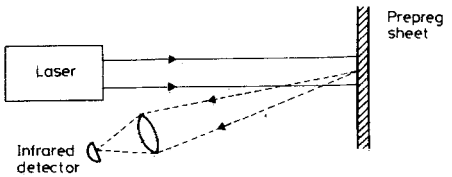

Fig. 1 Schematic diagram of the experimental setup

avoid major degradation of the heated surface. An infrared detector focused to the center of the heated area continuously monitors the surface temperature fluctuations. In our experiments a 1 mm-thick prepreg sheet was heated by either a 2 watt Argion-ion laser or a 100 watt CO_2 laser beam, or simply an inexpensive quartz-halogen lamp, and the infrared detector was an InSb photodiode. Longer-wavelength detectors such as HgCdTe or uncooled devices such as a thermopile or a pyroelectric detector could as well be used.

In the absence of curing, and for a constant radiative heat input, the surface temperature increase as monitored by the detector is of the kind of curves *b* or *c* in Figure 2. The temperature stabilizes at a saturation temperature at which the heat input equals the conduction heat flow within the material plus the surface radiative and convective losses. If the material is still uncured, a curve such as curve *a* in

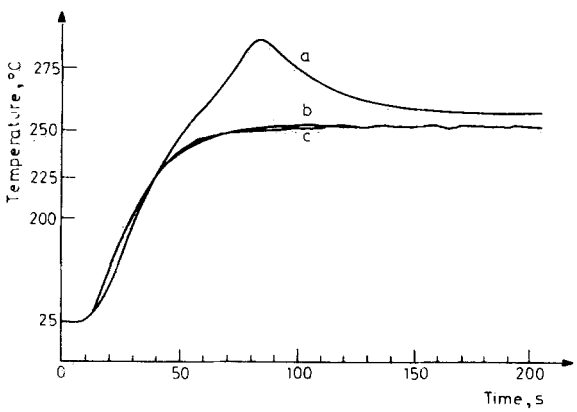

Fig. 2 Surface-temperature increase for a graphite-epoxy prepreg sheet tested with the apparatus shown in Figure 1. (*a*): first heating cycle; (*b*) and (*c*): second and third heating cycles

Figure 2 will be observed, the additional temperature level corresponding to the exothermic polymerization reaction. From the shape of the thermal curve one can thus evaluate the polymerization state of the prepreg.

The behaviour of a prepreg sheet in a more advanced state of cure was analyzed by submitting a sample to a two-step heating cycle. As shown in Figure 3, the first

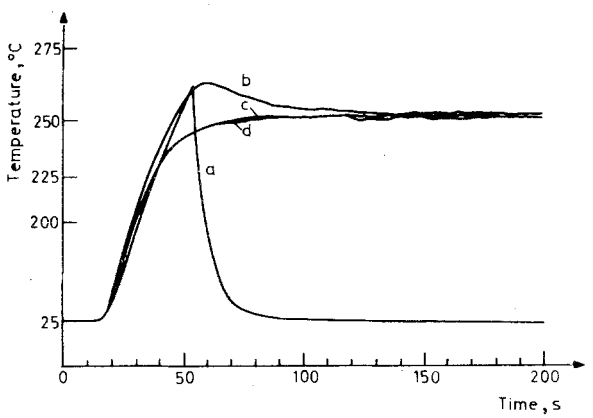

Fig. 3 Thermal curves corresponding to a two-step polymerization of a prepreg sample. (*a*) first heating cycle, producing a partial polymerization; (*b*) second heating cycle, producing a full polymerization; (*c*) and (*d*) third and fourth heating cycles, used as reference

heating cycle (curve *a*) was interrupted to produce a partial polymerization of the prepreg sample. After cooling to near-ambient temperature, a second heating cycle (curve *b*) was performed to complete the curing reaction, followed by two additional cycles (curves *c* and *d*) to be used as reference. The exothermic peak in curve *b* of Figure 3 is significantly smaller than in the corresponding curve *a* of Figure 2, indicating a more advanced polymerization state in the former case.

Discussion

The exact shape of the thermal curve depends on a number of parameters such as the geometry and thermal anisotropy of the heated sheet, the diameter of the laser beam, the air-flow-dependent level of the surface losses, etc. An absolute analysis of a single curve would thus be much more involved in this case as compared to the DSC case where a small sample is cut from the sheet and subjected to a well-controlled temperature program within an oven. On the other hand, such an absolute analysis should be repeated for every variation of the sample geometry or ambient ventilation level. In order to apply this technique to routine quality control on the industrial floor, such as on assembled parts of different geometries after autoclave curing, we thus propose a differential approach by which the same surface is repetitively submitted to heat cycles. As shown in Figure 2, the difference between the curves corresponding to two successive heat cycles gives a clear, although qualitative, indication of whether the material is incompletely cured (curves *a* and *b*) or has completely cured (curves *b* and *c*).

A quantitative estimation of the fractional extent of curing of the inspected material requires a knowledge of the sample geometry and thermal properties in order to calculate the heat of the reaction from the thermal curves. Such a calculation can be made for a given geometry if the processed parts have reproducible characteristics, or more simply an empirical calibration can be made on a series of samples whose degree of curing has been determined by a more quantitative physico-chemical analysis.

A practical device based on this approach could be implemented in a variety of configurations. A reflective cavity [14, 15] could be used for low-absorptivity materials such as white-painted CFRP structures or sandwich resin materials between aluminium sheets to assure a nearly 100% surface absorptivity and emissivity conditions for the quantitative analysis. Beam-shaping conical optical elements [16, 17] may be introduced along the laser-beam path to obtain a more uniform temperature distribution across the heated area. This would reduce the time-spread of the developed heat of reaction produced by a radially-expanding polymerization ring. An effect of this kind is shown in Figure 4, where the lower heating temperature results in a lengthening of the exothermic peak both because of a decrease in the reaction rate and of the radial expansion of the polymerizing volume.

Finally, the very small thermal inertia of such a non-contact method as compared to a thermal-contact DSC approach makes it possible to implement servo-loop, constant-surface-temperature techniques for reaction-heat evaluation without overheating. In such a case the surface temperature is quickly raised to an optimum polymerization temperature which is maintained constant for the observation period by suitably modulating the heat-source power using the detector output in a

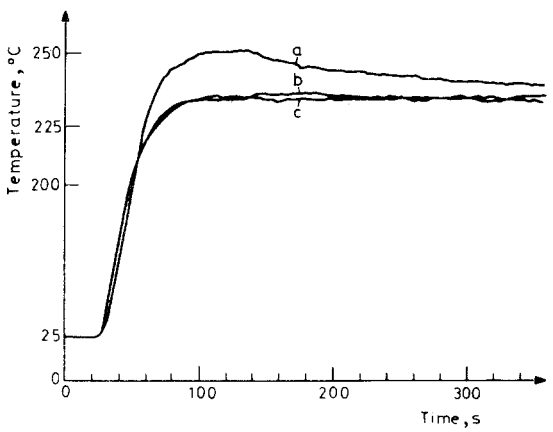

Fig. 4 Thermal curves similar to those shown in Figure 2, but at a lower laser power. Curve *a*: first heating cycle; curves *b* and *c*: second and third heating cycles

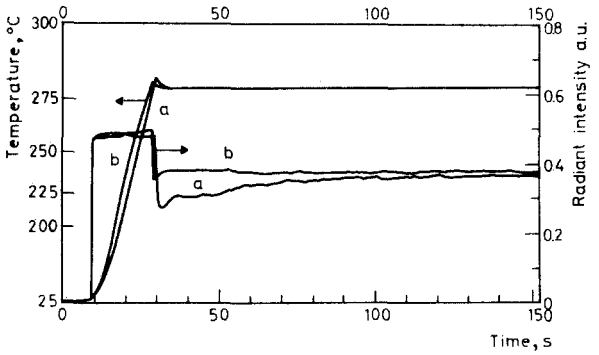

Fig. 5 Surface-temperature and heating-lamp output signals obtained with a prepreg in an (*a*) uncured and (*b*) cured state using a servo-loop approach

feedback loop. The output signal is in this case the time evolution of the heat-source power. Figure 5 shows an example of experimental curves obtained using such an approach. The power of the heating lamp was in this case modulated by a proportional-integral-derivative (PID) programmable controller set for a stable temperature level of 275°. The slight initial overshoot of the temperature curve is due to the unavoidable underdamping of a fast-reacting feedback loop. The output signal is the radiant intensity from the heating lamp as monitored by an optical detector. The difference between the uncured (*a*) and cured (*b*) output curves is evident, but further experiments have to be done to quantify the smallest difference in cure which can be distinguished by this optothermal method.

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Zusammenfassung — Es wird eine Nonkontaktmethode zur möglichen Anwendung für industrielle Routinebestimmungen des Vulkanisationsgrades von Polymergemischen beschrieben. Die Oberfläche der Probe wird durch einen Laserstrahl oder durch eine andere Strahlungsquelle erhitzt, wobei das Temperaturverhalten durch einen Infrarotmonitor kontinuierlich verfolgt wird. Ist das Metall partiell oder vollkommen vulkanisiert, kann man ein stark exothermes Signal beobachten. Durch Probengeometrie oder Umweltbedingungen verursachte Signalformänderungen werden durch eine Differentialnäherung mittels Vergleich aufeinanderfolgender Erhitzungszyclen an der gleichen Stelle minimal gehalten. Es werden einige Ergebnisse von vulkanisierten und unvulkanisierten Graphit-Epoxy Blättchen dargelegt.

Резюме — Описан безконтактный оптико-термический метод определения степени вулканизации полимерных композитных материалов для возможного его исполъзования в качестве обычного промышленного метода анализа. Часть поверхности образца нагревается лазерным лучом или каким-либо другим источником излучения, а выделяющаяся при этом теплота непрерывно измеряется приемником инфракрасного излучения. В случае композита, не подвергнувшегося или только частично подвергнувшегося вулканизации, наблюдается сильный экзотермический пик. Изменения формы сигналов, обусловленных изменением геометрии образца или окружающих условий, сводятся до минимума дифференциальным сравнением последующих тепловых циклов на том же самом участке поверхности. Представлены результаты, полученные с не- и вулканизированными графит-эпоксидными образцами в форме листов.