

Monitoring Cure in Epoxies Containing Carbon Nanotubes with an Optical-Fiber Fresnel Refractometer

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ABSTRACT: Fresnel refractometry was used to follow the changes in the refractive index during the isothermal curing of a simple difunctional epoxy resin, a commercial formulated multifunctional epoxy blend, and the same two resin systems modified by the addition of multiwalled carbon nanotubes. The refractive index change, monitored via an embedded optical fiber, was correlated with the degree of cure established from isothermal differential

scanning calorimetry measurements. A good correlation was established in all cases, indicating the potential of the technique to be used for online cure monitoring in thermosetting resin carbon nanocomposites. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 730–735, 2009

Key words: curing of polymers; nanocomposites; phase separation; refractive index; sensors

INTRODUCTION

The use of the refractive index as an indicator of the extent of cure in organic thermosetting resins has been reported by several authors.^{1–4} The technique has been established as being suitable to follow the changes from the liquid state to the solid state, *in situ*, in both resins and fiber-reinforced composites.^{5–7} The question arises whether it is still a suitable monitoring technique if the resin is modified by the addition of a relatively low concentration of an opaque nanoscale additive, such as carbon nanotubes (CNTs). This is the question addressed by the study presented here.

Thermosetting nanocomposites are in the stage of passing from the laboratory to real applications,^{8–11} and thus the need to be able to follow how they cure is likely to arise in the very near future. At present, dielectric cure monitoring is the best established of the potential online cure monitoring techniques,^{12–14} but the highly electrically conductive nature of CNTs is a contraindication for its practical

application in such compounds. In light transmission terms, even a very low concentration of CNTs will make the resin completely opaque, and this rules out other monitoring options such as infrared spectroscopy. The Fresnel refractometry technique used in this study^{4,6} probes the interface between the end of the embedded optical fiber and the curing resin and thus has the potential to be unaffected by the presence of the CNTs while still being sensitive to the changes taking place in the resin while it cures.

EXPERIMENTAL

Liquid-stage preparation of the nanocomposites

The simpler of the two epoxy resin systems used, which could be considered a laboratory model system, was based on the commonly used liquid diglycidyl ether of bisphenol A (Araldite MY750, Vantico, Ltd., Basel, Switzerland). The curing agent was a liquid aliphatic polyamine, polyoxypropylene diamine, with the commercial name of Aradur HY5922 (Fig. 1). It was used with the stoichiometric weight ratio of 55 parts per 100 parts of epoxy resin. The control sample was produced through the mixing of these components at room temperature for 15 min and then was subdivided into several plastic containers and stored at -18°C for further use.

A commercial CNT-epoxy premix (CP1204, Hyperion Catalysis International, Inc.) was used for the preparation of the corresponding nanocomposites. The premix contained multiwalled CNTs (3.06 wt %) predispersed in a mixture of two difunctional

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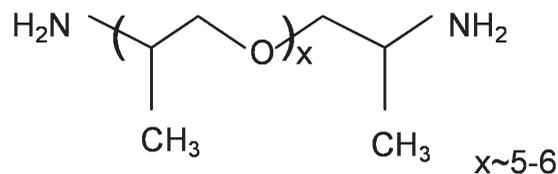


Figure 1 Chemical structure of the Aradur HY5922 curing agent.

epoxy resins with different monomer molecular weights, namely, Epon 828 and Epon 1009 F, in a weight ratio of 4.6/1. To make the nanocomposite master batch, the epoxy monomer liquid was first preheated to about 70°C to reduce its viscosity. A carefully weighed amount of the Hyperion premix was added to the warm resin and mixed into it with a Dispermat (VMA-Getzmann GmbH, Reichshof, Germany) CN F2 high-shear mixer at room temperature for 40 min at 5000 rpm. The amine hardener (HY5922) was then added to achieve the required 55/100 weight ratio, as in the control system. The mixing process continued for another 10 min. The final master batch had a CNT content of 0.06 wt %, and its samples were stored in individual plastic containers at -18°C for further processing.

The cryofractured surface of a cured sample shown in Figure 2 displays separated nanotubes, suggesting that a reasonable dispersion of the nanotubes was achieved in the master batches and persisted through the cure. Nevertheless, it is clear that clusters of nanotubes must also be expected to be present in the final nanocomposites.

The second epoxy system used in this investigation was a commercial formulated aerospace-grade resin called MTM 44-1, a product of the Advanced Composites Group (Derby, UK). It is described as a dual-cure-temperature and high-performance epoxy matrix. As such, it is representative of the types of complex blended resin systems used widely in the aerospace composites industry. The primary components are stated to be a tetrafunctional epoxy, two aromatic polyamines as curing agents, and a toughening additive. The multiwalled CNTs used to produce the nanocomposite master batch in this case were supplied by Thomas Swan Co. (Consett, County Durham, UK; Elicarb product reference SP7269 and batch reference K1005). The dry CNTs were dispersed in ethanol in a sealed plastic container and subjected to ultrasonication in an Elmasonic S30H ultrasonic bath at 60°C for 60 min. After the ultrasonication treatment, the container was opened and placed in an oven at 80°C for 20 min to evaporate the solvent, and this resulted in the production of a CNT cake. The resin was heated on a hot plate to 80°C and held there for 10 min to arrive at the minimum viscosity. On the basis of our own calorimetric data from differential scanning calorimetry (DSC) experi-

ments, no significant curing reaction was expected to occur in this resin at this temperature (the minimum curing temperature for this resin suggested by the manufacturer is 130°C for 4 h; the alternative is 180°C for 2 h). Accurately weighed portions of the CNT cake were added and mixed in with a spatula at 80°C for another 15 min. Given the high viscosity of this resin, even at its minimum viscosity level, it was not practical to use an electric stirrer. One master batch was prepared, containing 1 wt % CNTs. It was sealed in a plastic container and immediately placed in a freezer at -18°C. The high viscosity of the mix and the low temperature were expected to limit any reaggregation or settling of the nanotubes. The defrost procedure was always carried out with the container closed until it came up to room temperature to prevent the condensation of water. Manual remixing of the defrosted content was carried before any further sampling.

Thermal analysis

A TA Instruments (Wilmington, DE) 2920 temperature-modulated differential scanning calorimeter was used for the determination of the degree of cure achieved after a given time of cure in selected isothermal cure experiments. The experimental procedures were established and validated in our previous studies of a range of epoxy systems.^{15,16} The sample was first heated to the desired temperature at a heating rate of 20°C/min and then left to cure at the selected temperature. A simple horizontal baseline was used for the determination of the total heat of reaction.

A Bohlin (Malvern, Worcestershire, UK) CVO 120 HR high-resolution fluid-to-solid rheometer was used for viscosity measurements in an oscillating parallel-

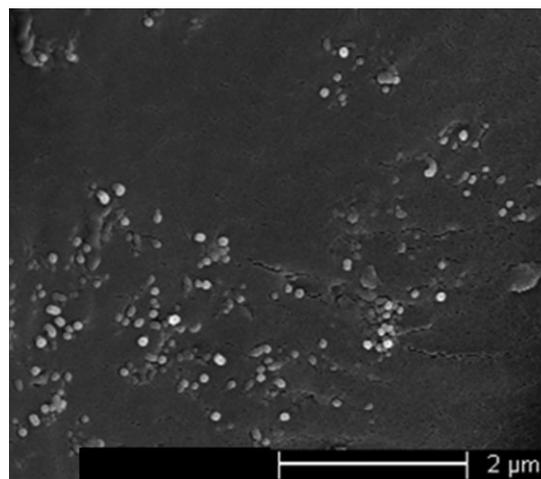


Figure 2 Scanning electron microscopy image of the cold-fracture surface of the MY750/HY5922 resin system containing 0.06 wt % Hyperion CNTs after curing at 120°C for 2 h.

plate configuration at a frequency of 1 Hz. After the plates were preheated to the desired temperature of the isothermal experiment, the sample was placed on the lower plate, and the upper plate was lowered to make contact with the resin. The experiment was started after the system was allowed to come to thermal equilibrium (typically 2–3 min) before any significant reaction occurred. The time between the onset of the rapid increase in the viscosity and the cure time at which the dynamic viscosity exceeded 10 kPa s was taken as the gelation period.¹⁶

Optical instrumentation and analysis

The configuration of the instrumentation used to measure the refractive index change during the curing reactions of the resins is shown in Figure 3.

The output from the laser diode operating at the appropriate wavelength was intensity-modulated and coupled into a network of directional couplers. The Fresnel reflection from the fiber/resin system interface was monitored with photodiode PD1. In the second arm, photodiode PD2 monitored the reflection from the air/optical fiber interface, acting as an intensity reference to aid the normalization of the signal and to account for any change in power coupled into the optical fiber from the laser diode. The outputs from the photodiodes were monitored with lock-in amplifiers. The refractive index determined with the refractometer (n) is given by the following equations⁶:

$$n = n_{\text{effco}} \frac{1 - \frac{\Delta}{\sqrt{R}}}{1 + \frac{\Delta}{\sqrt{R}}} \quad (1)$$

$$\Delta = \frac{n_{\text{effco}} - n_a}{n_{\text{effco}} + n_a} \quad (2)$$

$$R = \frac{V_{\text{air}}}{V_{\text{epoxy}}} \quad (3)$$

where n_{effco} is the effective refractive index of the fiber mode, n_a is the refractive index of air (1.0002739), V_{air} is the voltage produced by photodiode PD2 (obtained for the reflection from the fiber/air interface), and V_{epoxy} is the voltage produced by photodiode PD1 (corresponding to the reflection from the fiber/resin interface). All these values were calculated with the value of the effective refractive index of the fiber mode taken to be 1.456 at the operating wavelength of 800 nm. This value was determined by the immersion of the fiber end into a series of Cargill refractive index oils and by the observation of the refractive index at which the reflection from the fiber end was reduced to zero.

For the correlation between the refractive index and the state of cure of the resin systems used,

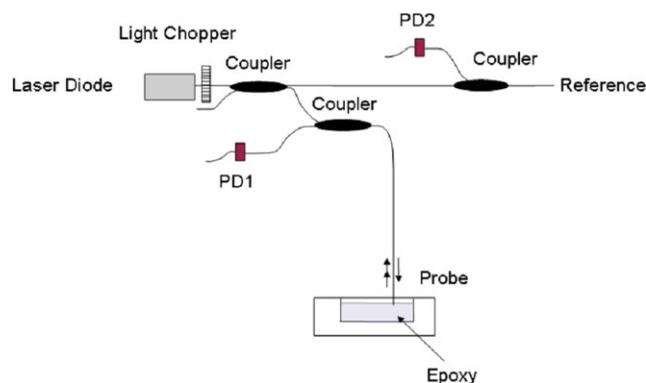


Figure 3 Experimental configuration used for the measurement of the refractive index change during cure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Cusano et al.² defined the term a_n which could be considered as “optical degree of cure,”:

$$a_n = \frac{n_t - n_0}{n_\infty - n_0} \quad (4)$$

where n_t is the refractive index at time t after the start of cure, n_0 is the refractive index at the beginning of cure, and n_∞ is the refractive index at the end of the cure. Equation (4) assumes a linear relationship between the degree of cure and the refractive index during the entire course of the cure. Equation (5) then relates the refractive index measurements to the real conversion values determined by the DSC experiments:

$$\alpha(T) = a_n \alpha_{\text{DSC}}^{\text{max}}(T) \quad (5)$$

where $\alpha(T)$ is the fractional conversion at time t for an isothermal cure at temperature T and $\alpha_{\text{DSC}}^{\text{max}}(T)$ is the maximum conversion attainable at temperature T .

RESULTS AND DISCUSSION

MY750/HY5922 nanocomposite

The simpler of the two resin systems, MY750/HY5922, was cured at 80°C for 6 h. Figure 4 illustrates the evolution of the degree of cure for the resin system and its nanocomposite containing 0.06 wt % Hyperion CNTs. In both cases, the evolution of the absolute refractive index value with the cure time parallels closely the progress of the chemical reaction, as indicated by the degree of cure determined from the DSC measurements. The refractive index data for the CNT-containing system [Fig. 4(b)] exhibit rather more scatter than the equivalent data for the neat resin. The correlation coefficient between the two entities is 0.998 for the neat resin (Fig. 5) and 0.974 for the nanocomposite. The absolute values of the refractive index start at 1.5019, corresponding to the uncured neat resin,

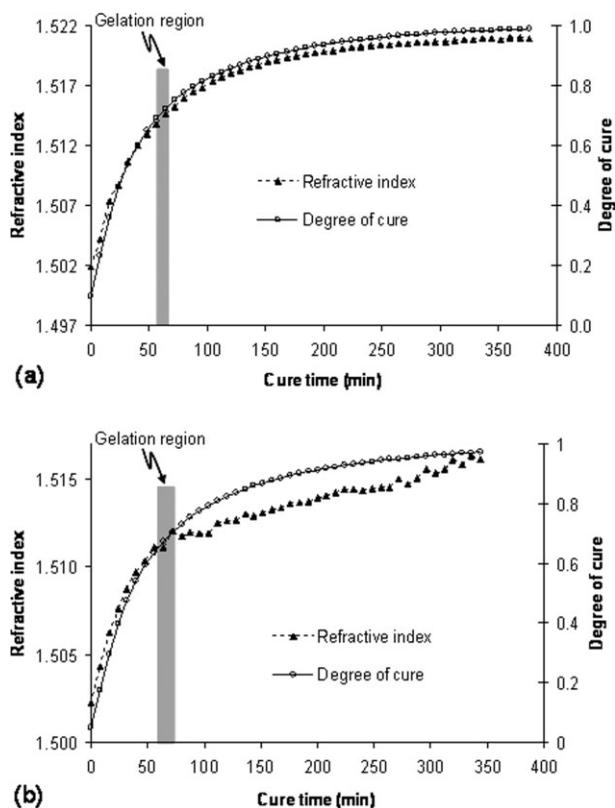


Figure 4 Comparison of the refractive index and degree of cure (based on the isothermal cure experiments) for the isothermal cure of (a) the MY750/HY5922 system and (b) the MY750/HY5922 system containing 0.06 wt % Hyperion CNTs at 80°C for 6 h (1550 nm).

and go up to 1.5201 for the fully cured resin, whereas for the nanocomposite, the values are 1.5025 and 1.515, respectively; all values are above the refractive index of the optical fiber.

The position and extent of the gelation region in terms of the cure time have been estimated from independent rheological measurements carried out under the same cure conditions. In Figure 6, the

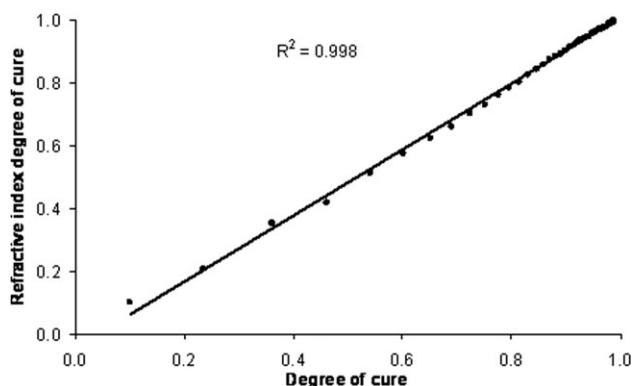


Figure 5 Correlation between the degree of cure and the degree of cure established from the refractive index measurements for the isothermal cure of the MY750/HY5922 system at 80°C for 6 h (1550 nm).

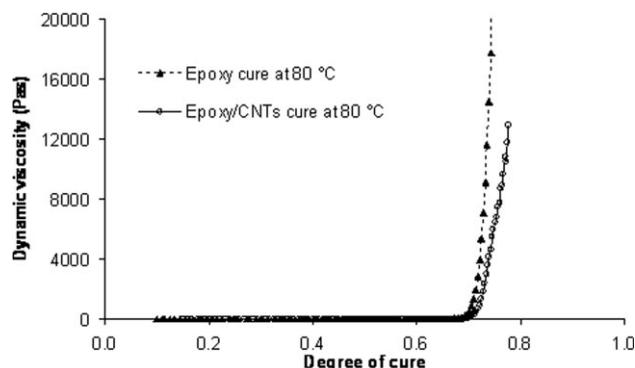


Figure 6 Dynamic viscosity advancement versus the degree of cure for the isothermal cure of the MY750/HY5922 resin system and its nanocomposite containing 0.06 wt % Hyperion CNTs at 80°C.

onset of the rapid increase in the dynamic viscosity is taken to indicate the onset of gelation.

The absolute value of conversion at which the system appears to gel is 72%. This is considerably higher than the value of 56% that would be expected from classical theory in this system.¹⁷ This could be a real effect, given the highly flexible molecular

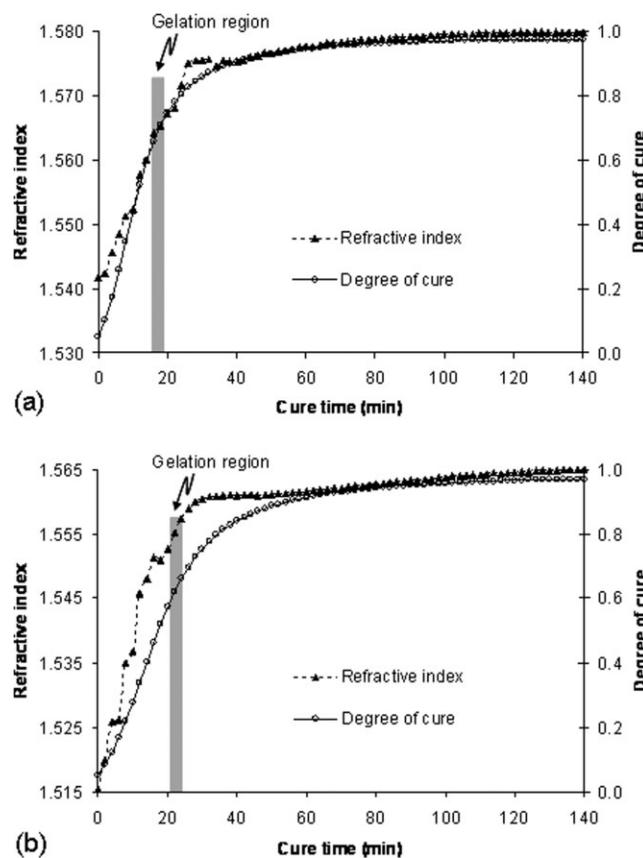


Figure 7 Comparison of the refractive index and degree of cure (based on the isothermal cure experiments) for the isothermal cure of (a) the MTM 44-1 system and (b) the MTM 44-1 resin system containing 1 wt % Thomas Swan CNTs at 180°C for 2 h (1550 nm).

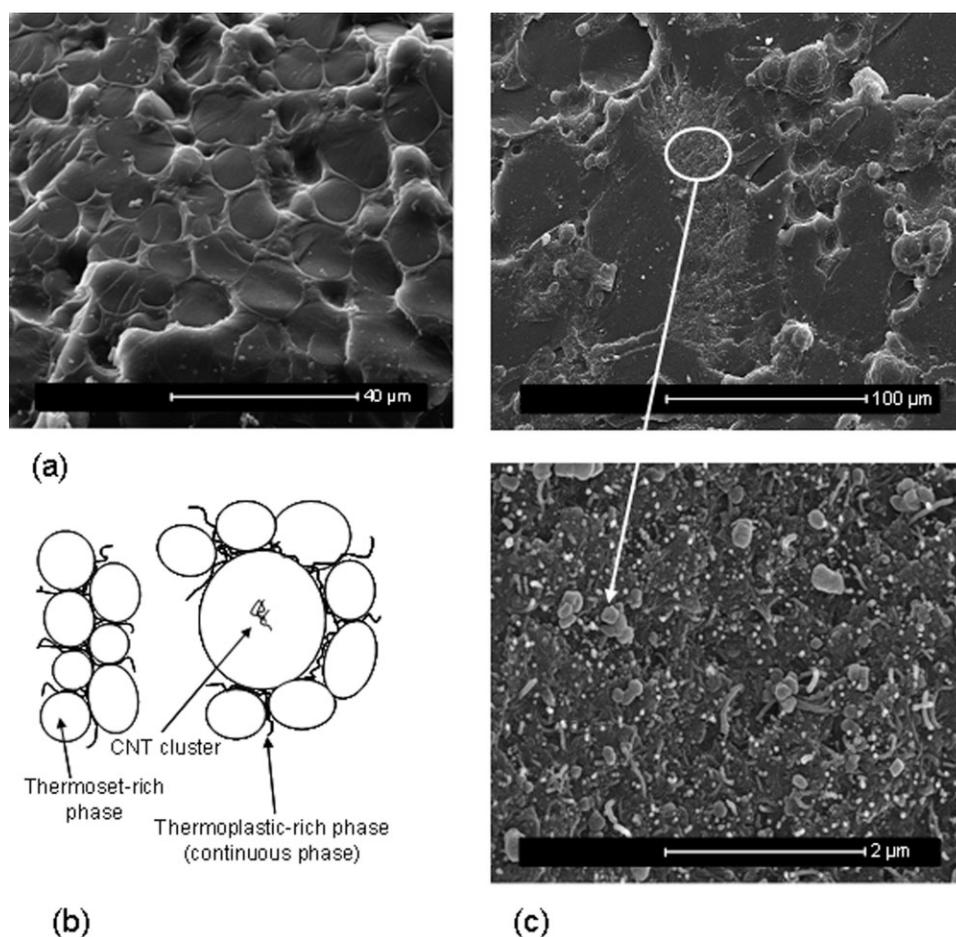


Figure 8 (a) MTM 44-1 resin system without the incorporation of CNTs, (b) schematic representation of the system with and without the incorporation of CNTs, and (c) MTM 44-1 resin system with the incorporation of 1 wt % Thomas Swan CNTs after curing at 190°C for 2 h.

structure of the hardener, or it could be an artifact of the measurement method, the dynamic viscosity being just one particular manifestation of molecular mobility within the crosslinking network. An independent determination of gelation was attempted by a previously established dielectric measurement method,^{12,18} but it was not successful in this system.

MTM 44-1 nanocomposite

Isothermal cures were carried out at 180°C for 2 h for the MTM 44-1 resin system and its nanocomposite containing 1 wt % Thomas Swan CNTs. The embedding of the optical-fiber sensor was rather more difficult in this resin because of the high initial viscosity of this blended system at room temperature. The resin was heated to 80°C for 5–10 min to reduce the viscosity sufficiently to allow the penetration of the fragile fiber sensor without it being damaged but not set off the chemical cure reaction. The sample was then allowed to cool to room temperature before the cure experiment was started. The results are shown in Figure 7.

The onset of gelation in the neat resin was determined by viscometry to occur at about 70% conversion. As the composition of this resin is not known, it is not possible to estimate any theoretical gel conversion. The same level of conversion was therefore assumed to lead to gelation in the nanocomposite. The fact that gelation occurs at a longer isothermal cure time in the nanocomposite is consistent with the observation of a perceptible slowdown of the chemical reaction through the presence of the nanotubes in this resin system.¹⁹ The effect of nanotubes on the cure process itself is outside the scope of this article and will be covered in future publications. The identification of the distinct stages of cure here is important only to evaluate the potential of the optical cure monitoring technique to follow the progress of cure in a practical manufacturing scenario.

Both the neat resin and nanotube-modified samples gave rise to a noisy signal from the start of the reaction up to gelation. The refractive index of the uncured neat epoxy system was 1.5420, rising to 1.5798 at the end of the curing reaction. For the nanocomposite, the values were 1.5153 and 1.5650, respectively. There are

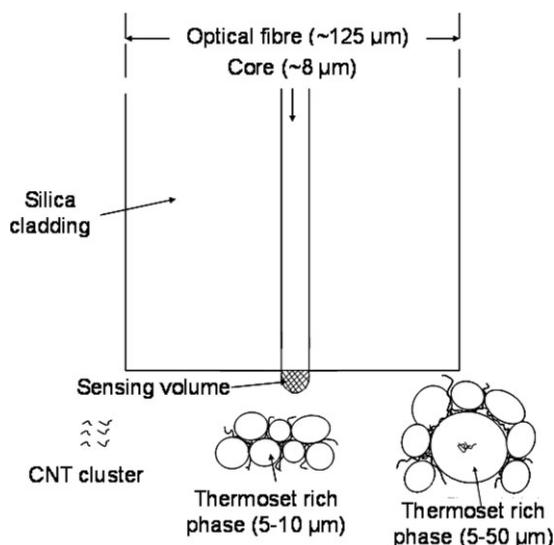


Figure 9 Schematic of the optical fiber embedded into the MTM 44-1 resin system and its nanocomposite containing 1 wt % Thomas Swan CNTs.

numerous possible reasons for the noisy signal obtained from the optical sensor. First, the range of values of the refractive index is above those measured in the simpler, one-component model resin system and thus even further away from the preferred measurement range of the sensor. However, it could also be the result of the movement of tiny air bubbles, which would be expected to be stopped by gelation. Although every care was taken to degas the resin samples, this is practically very difficult in this high-viscosity system, and the presence of trapped small bubbles is a realistic probability. Furthermore, in this blended resin system, cure-induced phase separation leads to a highly heterogeneous two-phase structure in the solid state. Scanning electron microscopy images of cryofractures of the neat resin, presented in Figure 8(a), show thermoset particles with a size range of 3–13 μm embedded in a continuous matrix that is believed to be thermoplastic-rich. The incorporation of CNTs into this blend appears to result in an average increase in the thermoset particle size, now 5–50 μm , with the majority of the particles having a mean diameter of 8–10 μm [see Fig. 8(c)].

A diagrammatic representation of the particles with respect to the optical fiber is shown in Figure 9. It is not clear how far the sensing volume from the optical-fiber core extends, but mass transport on a size scale comparable to the diameter of the fiber has to be expected during the process of cure and phase separation. Thermal hotspots in curing thermosets have been well documented, brought about by slight inhomogeneities in the local resin hardener concentrations and hence inhomogeneities in the rate of cure. In addition, the localized viscosity in the thermoset phase will initially be lower than that

in the thermoplastic phase by perhaps an order of magnitude, coming closer together until all change is stopped by gelation in the thermosetting phase. Any accompanying movement of CNTs, CNT clusters, or indeed just the formation of particulate structures within this volume could be expected to result in some fluctuation in the signal.

CONCLUSIONS

This early study has indicated that cure monitoring via a fiber-optic Fresnel refractometer is a viable proposition for CNT-filled thermosets. The data show the need for significant improvement in the signal-to-noise ratio; however, this may not be possible if the sources of the noise are intrinsic to the behavior of the resin system. In terms of the desirable optical properties of the fiber itself, for the particular resins tested here, the refractive index range should be between 1.5 and 1.6.

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