Application of photon emission technique to the determination of micro-fracture behavior in glass fiber-reinforced epoxy matrix composite

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Abstract

A photon emission behavior in a notched plane woven fabric glass fiber-reinforced epoxy matrix composite has been examined through tensile testing of a single-edge-notched composite specimen. Emitted photons during the test were detected and a spectroscopic analysis was also performed on the detected photons to determine the source of the emission. Direct observation of the fracture process of the composite reveals that bundle unit fiber fracture occurs from a notch tip and the fracture accompanies characteristic load drop in the load-displacement curve. Photons are detected about 15–30 μs after the onset of the load drop, which corresponds to the photon emission occurring at the beginning of a bundle unit fiber pullout from the matrix. The emission mechanism is determined to be gaseous ionization discharging of nitrogen molecules, which are contained in ambient air, at a debonded interface. Application of DC potential to the specimen enhances photon intensity and the technique allows photon imaging. Detected photon imaging clearly shows the area of interfacial frictional sliding. It is concluded that the photon emission technique is effective tool to determine interface debonding and sliding behavior in glass fiber-reinforced epoxy matrix composite. © 2001 Published by Elsevier Science Ltd.

Keywords: Photon emission; Glass fiber-reinforced epoxy composite; Interface debonding and sliding; Photon emission process; Photon imaging

1. Introduction

For three hundred years it has been well known that photons are emitted during fracture of various solid materials [1], and photon emission behavior was applied to understand scientific mechanisms in various fields. More recently, fracto-emission behavior, e.g. the emission of photons, particles, ions and molecules, has been used to determine micro-fracture behaviors in fiber-reinforced plastic matrix composites, especially in a glass fiber-reinforced epoxy matrix composite. Researches demonstrated that photon emission of the composite is a direct means of detecting the micro fracture behavior in the composite [2–4]. The photon emission mechanism has been studied and the sources of the emission in the visible wavelength range during fracture of a glass fiber-reinforced plastic matrix composite are assumed to be (i) recombination of free radicals [5–8], (ii) gaseous discharging [9,10] and (iii) excitation by self emitted UV photons [10].

Although studies have been made on photon emission behavior and photon emission mechanism of a glass fiber-reinforced epoxy matrix composite, the emission is not well correlated with micro fracture behaviors because of a poor mechanical characterization of the photon emission tests [2,5]. This limits the application of the photon emission method to mechanical characterization of composites. The objectives of this study are to apply this technique into the detection of fracture in a woven fabric glass fiber-reinforced epoxy matrix composite and to understand the relationship between micro-fracture behavior and the photon emission event. In addition, a new technique for ‘photon emission imaging’ is also discussed. The glass fiber-reinforced epoxy matrix composite is used because the composite is well used for photon emission study.

2. Experimental procedure

2.1. Composite material

A plane woven fabric glass fiber (Nihondenki Glass Co. Ltd., Shiga, Japan [13])-reinforced epoxy matrix composite was used throughout. The chemical composition of the glass fiber was 55 wt%SiO₂−20 wt%B₂O₃−14 wt%Al₂O₃−3 wt%Na₂O−3.0 wt%K₂O−3.0 wt%Li₂O−1.0 wt%MgO−1.0 wt%CaO. Table 1 lists properties of the fiber and matrix [13,14]. Both have a high electric resistivity, 1.0 × 10¹¹
and $2.3 \times 10^{14} \, \Omega \, \text{m}$, respectively, and thus the electric conductivity of the composite in the present experimental condition could be assumed to be infinite. The plane woven glass fiber fabric was cut approximately $100 \, \text{mm} \times 100 \, \text{mm}$ square and eight sheets were stacked in the same fiber axial directions. The stacked sheets were put into a Teflon®-coated tray of which inner size was $120 \, \text{mm} \times 120 \, \text{mm} \times 10 \, \text{mm}$. The matrix material was a clear grade epoxy resin monomer (Epicote 828, Yuka-shell, Tokyo, Japan). The resin was cured using 46 wt% of curing agent (MH-700E, Shin-Nihon-Rika, Tokyo, Japan) and 0.27 wt% of accelerator (DBU, Sum-Apro, Tokyo, Japan). These three base components were mixed together in ambient air. Then, a mixture of an epoxy monomer was poured into the tray and evacuated at 333 K to remove air in the stacked sheets and the epoxy monomer under a vacuum of $\approx 10^{-2} \, \text{Pa}$ for 1.2 ks. The evacuated material was put into an oven and cured at 373 K for 4 h, after which the composite specimen was removed from the tray. Other details of the processing of the epoxy were reported elsewhere [15,16]. Dimensions of the as-fabricated composite were about $100 \times 100 \times 3 \, \text{mm}$ thick with a nominal fiber volume fraction $\approx 0.3$.

Fig. 1 shows a typical example of the appearance of the fabricated matrix and composite; the thickness of both materials was $1.0 \, \text{mm}$ ($\pm 0.1 \, \text{mm}$). The characters beneath the composite are legible, which means achievement of an optical transparency of the composite at a visible wavelength range. This optical transparency allowed direct observation of the fracture event inside the composite and thus fracture behavior inside the composite could be identified from the outside. It should be noted that the used epoxy matrix has optical transparency above wavelength longer than $300 \, \text{nm}$ [17] and this transparency was enough for the present spectroscopic analysis (wavelength range: 400–700 nm, resolution: 0.8 nm). Calibration of the spectrometer was done using He line series (wavelength: $\lambda = 545.9$ and 611.7 nm). Typical micrographs of the polished sections in the parallel and through-the-thickness planes of the composite are shown in Fig. 2. Due to the relatively low volume fraction of the composite, the fiber bundle and matrix phases are clearly identified from the surface of the composite.1

2.2. Specimen and fracture test

The composite panels were cut into a single-edge-notched (SEN) specimen, the shape and dimensions of which are shown in Fig. 3. To achieve good optically transparency of the composite, the surfaces of the specimens were polished to a $1 \, \mu\text{m}$ diamond paste finish. The notch was introduced by a $200 \, \mu\text{m}$ thick diamond cutting braid. The resultant notch width and tip radius were $\approx 250$ and $\approx 500 \, \mu\text{m}$, respectively. The ratio of the notch depth, $a$, to the width, $w$, of specimen, $a/w$, was fixed at $\approx 0.5$, which corresponded to an actual notch length of $\approx 4.5 \, \text{mm}$. A pure epoxy specimen with shape and dimensions identical to that of the composite specimen was also prepared to examine photon emission behavior.

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1 The poor contrast of the optical micrographs is due to a small difference of the refractive index between the fiber and matrix which is important to achieve optical transparency of the composite [19,20].
Tensile tests of both the composite and pure epoxy specimens were carried out using an Instron testing machine (Model 4208, Instron Corp., NJ, USA) at room temperature (297 K) in ambient air with a constant crosshead displacement rate of $1.2 \times 10^{-7}$ m/s. The tensile direction of the composite was aligned to one of the fiber bundle directions. Tests were done inside an optical shield box to allow detection of photons emitted during the test. For the selected composite specimens, the damage progress in a ligament area was directly observed using a low magnification video-microscope (Model KTS-100, Kenko, Nagano, Japan). In this case, the test was done under white light illumination; therefore no detection of photon emission was attempted. The light reflection technique allowed direct observation of interface debonding and pullout behaviors [18,19]. More than ten specimens were used for each kind of test to obtain common fracture and photon emission behaviors. After the test, the fracture appearance and fracture surface were observed by scanning electron microscope (SEM).

### 2.3. Photon detection and spectroscopy

Fig. 4 shows a schematic illustration of the two photon detection systems used in the present study; (i) photon counting and (ii) photon spectroscopy. By both techniques, the photons emitted from a circular area ~8 mm in diameter, the center of which was located at the notch tip, were detected (detected area is shown in Fig. 3). Photons were counted by a photomultiplier (Model H5783-03, Hamamatsu Photonics Corp., Hamamatsu, Japan), in which the detected area was positioned ~10 mm away from the specimen surface. The photomultiplier had a detectable wavelength range from 185 to 650 nm with maximum sensitivity at a wavelength of 420 nm [20]. The output signal from the photomultiplier was transferred to an ultra high-sensitivity electric current meter (Model TR8652, ADVANTECH, Tokyo, Japan). The signal was integrated every 20 ms and the output signals from the electric current meter were transferred to a digital data acquisition system.

Photons collected by an optical microscope (BUH, Olympus Co. Ltd, Tokyo, Japan) were guided into an optical fiber bundle (total diameter: 1.0 mm) and the opposite end of which was connected with a monochromator (Spectra Pro. 275, Acton, NJ, USA). The nominal resolution of the monochromator was less than 0.8 nm at a wavelength of 500 nm. Photon emission spectrum at the wavelength range from 400 to 800 nm was monitored with an exposure time of 0.5–0.6 s for one flame. The photons from the monochromator were detected by a high sensitivity CCD camera (576 x 384 pixels, 576-G1, Princeton Instruments, NJ, USA) with a frame speed of 1ms per spectrum. The spectrum was continuously stored in a personal computer and then analyzed using commercially available software (Win Spec 1.4.3., Princeton Instruments, NJ, USA). The effect of applying DC potential on the photon emission behavior was examined because the reports suggested that a strong candidate for the photon emission process is discharging at the fracture surface and gaseous ionization–nucleation process originating from the discharging [9,10,21]. Thus, the application of potential is expected to allow enhancement of photon emission signals. To apply DC potential, $V_a$, near a notch, rectangular Cu strip electrodes (thickness: 0.2 mm, width: 5.0 mm) were bonded to the specimen, the location of electrode is shown in Fig. 5. The maximum applied DC potential was selected at 500 V.
2.4. Photon imaging

Photon imaging was carried out using an ultra high-sensitivity black and white film (GX3200, Konica, Japan, the nominal sensitivity of the film: ISO number 3200). In this case, a conventional 35 mm camera was used with a commercially available lens. The possible imaging area was 5.1 x 0.4 mm² on the film. The lens (F = 2.0) was located opposite to the optical microscope; the distance between lens surface and specimen surface was ≈ 8.0 mm. Therefore, no photon counting was done with photon imaging, although the photon emission spectrum was monitored. During the fracture test, the shutter of the camera was kept open to allow imaging of emitted photons. After the test, the film was processed under sensitization development which allows increase of the film sensitivity up to ISO number 6400.

3. Results and discussions

3.1. Fracture behavior and photon emission

Typical example of a load-displacement record of a SEN composite specimen and the sequences of the direct observation result are shown in Figs. 6 and 7, respectively. As the composite has optical transparency, the fracture and damage regions of the composite from the notch tip are clearly distinguished as white damaged areas. Fracture of the composite at the notch root begins from a matrix cracking near a maximum load. This first matrix cracking occurs in a pop-in like manner and one unit fiber bundle fracture follows this pop-in like matrix cracking (Fig. 7(b)). The step-like load decrease after the maximum load corresponds to a step-wise bundle unit fiber fracture with an advance of matrix cracking; the load drop is well contrasted with a spread of the white area at a ligament (Fig. 7(c) and (d)). Fig. 8 shows a SEM photograph of the fracture surface of a composite near a notch tip. Bundle unit longitudinal fiber pullouts from the fracture surface are clearly observed and suggest progress of the interface debonding between the fiber and matrix, then subsequent frictional sliding at the interface during fracture process.

No effective photon emission is identified in a pure epoxy specimen within the sensitivity of the photon detection system used. On the other hand, clear photon emission signals are identified in all the tested composite specimens. Fig. 9 shows a typical load-displacement curve of SEN specimen with the detected photon emission counts for the specimen without DC potential ((a): V_d = 0 V) and with DC potential ((b): V_d = 500 V). The emission occurs spontaneously with respect to the load and most of the photons are detected just after the load drops in the curve. Detailed analysis shows about a 15–30 µs time lag is observed between the load drop and the photon emission event (Fig. 10, the data area is shown in Fig. 9 by broken line square). As shown before, direct observation result near the notch tip reveals these load drops are caused by a bundle
unit fiber fracture and following bundle unit fiber pullout; suggesting that the photon emission behavior is strongly correlated with the beginning of fiber pullout from a cracked matrix.

The figure also shows the application of DC potential increases both photon emission event and emitted photon intensity. Fig. 11 shows plots of total photon intensity versus applied DC voltage. Here, total photon intensity, $I_{\text{total}}$, during fracture is defined as

$$I_{\text{total}} = \int_{0}^{t_{f}} I_{\text{PE}}(t) \, dt,$$

where $t_{f}$ is time of fracture and $I_{\text{PE}}$ is photon emission intensity at time $t$. Because of the limited number of tests, accurate relation between $I_{\text{total}}$ and applied voltage is difficult to determine, although it is clear that $I_{\text{total}}$ becomes larger with the increase of applied voltage. The effect of DC potential on the photon emission behavior will be discussed later.

### 3.2. Origin of photon emission behavior

A typical example of the photon emission spectra from the composite is shown in Fig. 12. Here, the spectrum is obtained at point ‘A’ in the load-displacement curve (Fig. 8(b)). Although, the noise level is relatively high, clear strong peaks are identified above the threshold level, and the wavelengths of these peaks are listed in Table 2 together with the identified electron transitions. The source of the wavelengths of these peaks is determined using spectroscopic tables [22–24]; most of the photons from the composite are identified as originated from the first positive band and the second positive band of the nitrogen molecule ($N_2$). The detected peaks $B_1^{-}B_3$ belong to the first positive band group of $N_2$ and the transition is given.
Fig. 12. Typical photon emission spectrum during fracture of composite.

by \(B_3\Pi_6 \rightarrow A_1\Sigma^+_g\) (Table 2). Peaks \(A_1\cdots A_{15}\) belong to the second positive band group of \(N_2\) by the transition \(C_1\Pi_u \rightarrow B_3\Sigma_g^+\). The nitrogen molecule is not contained in the fiber and matrix and thus the source of the emission is related to the test atmosphere because the experiment is done under ambient conditions.

It is known that the ionization mechanism of nitrogen molecules is as follows [9,10]

\[
e^− + N_2N_2^+ + e^− \rightarrow N_2N_2 + hν, \tag{2}
\]

where \(h\) is the Planck’s constant, \(ν\) is frequency and \(N_2^+\) indicates the excited state of nitrogen molecules. Such nitrogen-related peaks originate from gas-discharging process and the results of the present experiment are very close to the photon emission behavior reported during the peeling of magnetic tape from copper in air [11,12]. The photon emission occurs about 15–30 \(μs\) after the sudden load drop in the load-displacement curve. This process corresponds to just the beginning of a bundle unit fiber pullout stage from the matrix. When the interfacial relative sliding occurs, the roughness of the pair of debonded surfaces creates a condition of electric discharging. Then, local discharging at the debond interface near the cracked matrix surface creates a condition of excitation of nitrogen molecules. The excited nitrogen emits photons during its re-nucleation process. The result suggests that the photon emission process of the glass fiber-reinforced epoxy from \(N_2\) molecules is very close to that observed during the frictional sliding process of solids in air, i.e. tribo-emission behavior [1,25,26]. The existence of other possible sources such as \(O_2\), \(H_2\) and \(H_2O\), however, is still unclear within this study.

3.3. Photon emission image

Fig. 13 shows an example of an emitted photon image during a fracture experiment of the SEN composite specimen. In this case, DC potential (500 V) is applied to the specimen to enhance photon emission intensity because the application of electric charge is a strong tool to increase photon intensity during the fracture experiment of a glass fiber-reinforced epoxy matrix composite (Fig. 11). The location of the notch tip is also indicated in the photograph. The photon image is located along the crack path of the composite and the width of the photon-detected area is nearly the same as fiber pullout length from the fracture plane. This evidence suggests that the detected photon image corresponds to the micro fracture behavior: especially, fiber pullout behavior. A strong photon image (white area) is located just ahead of notch tip. Diffusion of the photon image is probably due to a scattering of photons, emitted inside the specimen. As the composite contains eight ply woven fabric sheets, the photons from inside the specimen are detected and cause a spreading of the detected photon image, i.e. the location spreads along crack path. The above result demonstrates the possibility of photon imaging during the fracture experiment of a glass fiber-reinforced composite.

4. Conclusions

Photon emission count and spectroscopy were performed during a fracture experiment of a notched woven fabric glass fiber-reinforced epoxy matrix composite. Photon imaging was also carried out during the fracture test. It is found that the photon emission occurs just after the progressive load drop in the load-displacement curve of the
composite with a time lag of 15–30 μs. The load drop originates from a bundle unit fiber pullout and the photon emission is associated with the beginning of fiber pullout from the cracked matrix. During the pullout process, nitrogen molecules in ambient air existing at a frictionally sliding interface are excited by electron bombardment at frictionally sliding interface and photon emission occurred during the re-neutralize process of the excited nitrogen molecules.

The application of DC potential increases emitted photon intensity because the emission originates from a discharging of nitrogen molecules at the frictionally sliding interface. Photon emission imaging is successfully obtained by applying electric potential during a test because the emission is enhanced by application of the electric potential.

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