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Original Article

Deformation behavior of release agent coated glass fibre / epoxy composite using carbon nanotubes as strain sensors

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Abstract

The deformation behavior of model glass fiber in epoxy composites has been studied using Raman spectroscopy properties. Single walled carbon nanotubes (SWNTs) were introduced at the glass fiber/epoxy interface as strain sensors, which can be detected by Raman Spectroscopy, to sense the strain profile of the fiber under deformation. The release agent was applied on the fiber surface before composite fabrication. It was found that at high strain level, the behavior of a single fiber in a composite did not follow a classical shear-lag model as shown in the fragmentation study. This is due to the interfacial failure caused by the release agent. The strain mapping result can be compared to that without release agent coating. The finding confirmed the application of SWNTs as strain sensors at the fiber/composite interface.

Keyword: SWNTs, strain sensors, fragmentation, release agent, raman spectroscopy

1. Introduction

Studying the deformation behavior in composite materials is very crucial, because the failure of composites after being loaded from external load is a main factor to be considered in order to use materials in different applications. Fiber-matrix adhesion is a key property in composite materials. The better the adhesion between fiber and matrix is the higher the strength of the composite materials. The key factor to control these properties in composites is the fiber/

*Corresponding author. Email address: fengpwn@ku.ac.th matrix interface. Interfacial adhesion can be determined by measuring interfacial shear stress (ISS) using micromechanical testing methods that employ different loading configurations giving rise to different values of ISS (Andrews *et al.*, 1996). In order to measure the ISS, samples are loaded until complete interfacial failure occurs. The values obtained from the tests depend on the quality of the interfaces as well as the matrix properties and they are a maximum at the broken fiber ends (Tripathi *et al.*, 1998).

One technique that has been used to study the deformation behavior especially at the fiber-matrix interface is the Raman scattering technique (Yallee *et al.*, 1998). Nevertheless, there is a limit of materials that can be used with this technique. Glass fiber is one of the fibers that does not give a well define peak. To study the deformation behavior of the glass fiber using Raman scattering technique was not possible. The micromechanical study of a glass fiber/epoxy composite system using Raman spectroscopy to follow the interfacial strain distribution of a glass fiber was first successfully studied using a diacetylene-urethane copolymer coated as a strain sensor on the fibers to map the strain distribution along the fibers during the fragmentation test (Young et al., 2001). After that, using the Raman spectrum of single walled carbon nanotubes (SWNTs) dispersed in a polymer matrix to sense the strain fields around the embedded glass fibers was successful (Zhao et al., 2003). Also, glass fibers containing a small quantity of samarium fluoride (SmF_2) were produced enabling luminescence spectroscopy to be detected in the same manner as Raman spectroscopy (Hejda et al., 2008). The deformation behavior was then studied through the luminescence spectroscopy set up from the Raman spectrometer. In this work, single walled carbon nanotubes were incorporated as they give a well define peak (Wood et al., 2000; Cooper et al., 2001; Sureeyatanapas et al., 2009; Sureeyatanapas et al., 2010). The deformation of the material then became possible. SWNTs were, in that case, used as strain sensor at the fiber/ matrix interface.

SWNT has been known as an excellent Raman active material. The SWNT Raman bands compose of a radial breathing mode (RBM) at 100-400 cm⁻¹, a defect induced mode at 1,300-1,500 cm⁻¹ (D-band), a tangential mode at 1500-1600 cm⁻¹ (G-band), and an overtone of the D-band at 2,500-2,700 cm⁻¹ (G'-band). The G'-band shifts significantly from its original position during deformation. It shifts to a lower wave number position when the SWNTs are under tension and to higher wave number position when the SWNTs are under compression (Wood *et al.*, 2000; Cooper *et al.*, 2001). Deformation of SWNTs can therefore be followed by monitoring changes in the Raman G'-band position.

In our previous work (Sureeyatanapas et al., 2009; Sureeyatanapas et al., 2010), the SWNTs were used to follow the strain along the model glass fibers treated with silane coupling agent in various ways of preparation methods. With the coupling agent, the SWNTs at the fiber/epoxy interface can follow the strain along the fibre length. The deformation behavior follows the classical shear-lag model (Nairn et al., 1997). Glass fiber/epoxy composites system has been widely applied in marine piping, chemical plants, aircraft and aerospace applications (Phillips et al., 1998). The fluorocarbon release agent is normally used to coat the surface in order to reduce the friction coefficient resulting in the reduction of bond strength (Hadjis and Piggott, 1977). The purpose of this work was to investigate the effect of applying release agent on the deformation behavior of the fiber in composites using SWNTs at the fiber-matrix interface as strain sensors. This work was then combine to the previous works (Sureeyatanapas et al., 2009; Sureeyatanapas et al., 2010) in which the coupling agent was applied onto the fiber in the same system. The behavior then can be explained in terms of adhesion properties at the interface of the fiber/matrix composites.

2. Research Methodology

2.1 Materials preparation

The 0.01% by weight COOH-SWNTs, purchased from Sigma-Aldrich Co., Ltd., UK, was firstly sonicated in ethanol solution for 2 hrs. Then the fibers were sized in the solution for 10-15 minutes followed by drying. This was done without silane coupling agent mixing, as in the previous work (Sureeyatanapas et al., 2009; Sureeyatanapas et al., 2010) to eliminate the effect of silane coupling agent on the application of release agent. The entire SWNTs sized fibers were sprayed with release agent before embedding a single fiber in the epoxy dumbbell shape specimen for fragmentation test. The release agent was Ambersil Formula 10, which is fluorocarbon polymers, purchased from Ambersil International Chemicals, UK. It is suitable for Polyurethane (PU), epoxy resins, polyesters and thermosets up to 180°C. Note that the glass fibers used in this study were made from the glass rod hot stretching, which the diameter was in the range of 50-150 micrometers. The larger fiber size allowed easier handling during the experiment when compared to the smaller size of commercial fibers. These glass fibers were found to have a mean Young's modulus of 80.8±6.9 GPa. The epoxy resin matrix was a mixture of Araldite resin LY5052 (butane-1,4 diol diglycidyl ether resin) and Aradur hardener HY5052 (isophorone diamine), purchased from Vantico, Polymer Specialties, UK. The mixing ratio was 100 parts of LY5052 to 38 parts of HY5052. The average Young's modulus was 2.77±0.17 GPa.

2.2 Mechanical property tests

Several single fibers were deformed in air to find the relationship of % fiber strain and Raman shift rate as a calibration curve before carrying out the fragmentation test. The shift of the G' band, in the 2,400–2,800 cm⁻¹ region, was followed during axial tensile deformation. This test is called 'a single fiber deformation test'. The details of sample preparation and testing were shown in our previous publication (Sureeyatanapas *et al.*, 2009). Then the fragmentation test was performed to investigate the strain profile along the fiber length using the % fiber strain from calibration curve to convert Raman band into % fiber strain. From this test, the deformation behavior of the fiber was obtained and the data was fitted with the classical shear-lag model and other models depend on the types of failure.

2.3 Shear-lag models

In the stress transfer process, the stress is transferred from the matrix to the fibers through a shear at the interface resulting in a stress distribution along the fiber length. An axial stress in a single fiber embedded in an infinite matrix can be predicted using the elastic shear-lag analysis. The famous shear-lag model was originally proposed by Cox (Cox, 1952). Cox's model is suitable for the strain distribution at low matrix strain levels ($\varepsilon_m < 1.2\%$). It does not account for matrix yielding and interfacial failure occurring in the highly stressed region at the fiber ends. However, the model predicted from Cox's model can be off by 10-20% and larger errors of interfacial shear stress can be 50-100% too high or too low for the system with modulus ratios between the fiber and the matrix of 100 and 10. Nairn modified the Cox's shear-lag model since some assumptions from Cox's model do not work for low volume fraction composites and the displacement boundary conditions there are incorrect (Nairn, 1997). Nairn's model gives reasonable estimation of the stress transfer and strain energy in a finite fiber in an infinite matrix composite. Nairn's model for calculating fiber strain (ε_f) and interfacial shear stress (τ) gives

$$\varepsilon_f = \varepsilon_m \left[1 - \frac{\cosh\beta\left(\frac{l}{2} - x\right)}{\cosh\beta\frac{l}{2}} \right]$$
(1)

$$\tau = E_f e_m \left[\frac{G_m}{2E_f \ln\left(\frac{r_2}{r_1}\right)} \right]^{\frac{1}{2}} \left[\frac{\sinh\beta\left(\frac{l}{2} - x\right)}{\cosh\beta\frac{l}{2}} \right]$$
(2)

where

$$\beta = \left[\frac{2}{r_1^2 E_f E_m} \left[\frac{E_f V_f + E_m V_m}{\frac{V_m}{4G_f} + \frac{1}{2G_m} \left(\left(\frac{1}{V_m} \right) \ln \left(\frac{1}{V_f} \right) - 1 - \frac{V_m}{2} \right)} \right] \right]^2$$

and $G_m = \frac{E_m}{2(1+\nu)}$

 $r_1 = \text{Fiber radius},$

 r_2 = Matrix radius around fiber,

$$V$$
 = Volume fraction; of matrix $V_m = \frac{r_2^2 - r_1^2}{r_2^2}$

and of fiber
$$V_f = \frac{r_1^2}{r_2^2}$$

In some cases, especially in high strain levels ($\varepsilon_m > 1.2\%$), the matrix system undergoes plastic deformation. Kelly and Tyson presented their model for stress transfer at high strain levels to include the effect of plastic yielding of the matrix, which started at the fiber end and then propagated along the fiber/matrix interface (Kelly *et al.*, 1965).

3. Results and Discussion

3.1 Fragmentation tests (standard)

The characterization of the COOH-SWNTs is not included in this paper as it was shown in our previous work (Sureeyatanapas *et al.*, 2009; Sureeyatanapas *et al.*, 2010). The COOH-SWNTs sized fibers, without the release agent sprayed, were first coated with epoxy and deformed in air to find the calibration curve. This is to model the glass fiber condition as that in the epoxy matrix. The average strain shift rate of fibers was -20.7 ± 2.9 cm⁻¹/% fiber strain as shown in Figure 1. The value was slightly lower than that with silane coupling agent addition (Sureeyatanapas *et al.*, 2009). The mapping result from COOH-SWNTs without silane addition and without release agent coating in the epoxy specimen is showed in Figure 2 as a comparison.

It can be seen that without silane agent, COOH-SWNTs can still follow the fiber strain and Nairn's shear-lag model can be fitted well with low scatter (Nairn *et al.*, 1997). As higher strain was applied, the fragmentation occurred. At



Figure 1. Relationship between fiber strain (%) and Raman G'band position (cm⁻¹) from a single fiber deformation test of 0.01% by weight of COOH-SWNTs in the sizing layer without silane addition and with the epoxy coating layer.



Figure 2. Mapping of COOH-SWNTs in the sizing layer without silane treatment in the cold cured epoxy/hardener specimen at (a) 0%, 0.3%, and 0.6% matrix strain.

0.3% matrix strain the measured strain near the right end of the fiber is slightly lower than the predicted strain. This may be due to stress relaxation of the epoxy matrix during measurement and/or time dependence of debonding process as the data collection started from the left end to the right end of the embedded fiber (Yallee *et al.*, 1998). When the higher matrix strain was applied, the fiber fractured more.

3.2 Fragmentation tests (with release agent)

In this fragmentation test, a release agent coated single glass fiber was embedded in epoxy specimen for deformation. Five specimens were tested and all have shown two behaviors as presented here. The first result is shown in Figure 3. It was found that fragmentation occurred in the third step of the applied strain together with the collapse or failure of the interface around the fracture points. At 0% matrix strain the fiber had no initial stress or strain while at 0.3% matrix strain the fiber showed elastic behavior followed Nairn's elastic shear-lag model (Nairn et al., 1997). At 0.6% matrix strain, the fiber fracture at positions 5.42 mm and 14.96 mm from the right end. The interfacial adhesion failed up to ± 5 mm around the fracture points where the fiber strain become zero which may be from the interfacial failure. However, at the middle area between the fiber fracture points followed the elastic shear-lag model (Nairn et al., 1997), which fitted well with the experimental data.

The variation of interfacial shear stress with distance along the fiber derived from specimen in Figure 3 is shown in Figure 4. It can be seen that ISS distribution at 0% and 0.3% matrix strains were consistent with the samples without release agent (Sureeyatanapas *et al.*, 2009; Sureeyatanapas *et al.*, 2010). However, around the fiber fracture area at 0.6% matrix strain, the fiber was fully-debonded at each fracture point and the ISS became zero. It then continued to be fully bonded at the middle area of the fracture point. The maximum ISS was around 15 MPa at the fiber ends and at the fracture points when the matrix strain is 0.6%.

From the optical microscope (not shown here) it can be seen that the fiber fractured during the deformation without matrix cracking. This indicates the occurrence of the interfacial failure. Raman data of fiber strain mapping can also confirmed that the fiber was debonded from the resin as it causes less effective stress transfer. Furthermore, at high strain levels there were debondings of SWNTs from the fiber in many positions along the fiber. The adhesion between the fiber and resin reduced significantly as observed at high strain level due to the release agent being applied. The examples of SWNTs sliding along the fiber-matrix interface were photographed and are shown in Figure 5. On the right, at high strain level, the stress was being transferred from matrix to the fiber and the SWNT, which could no longer handle the stress as the chemical bonding between the SWNT, epoxy resin, and glass fiber was weak. Therefore, at the initial stage, the SWNTs slide along the fiber as the bonding was broken. Later the fiber was subsequently broken as it could not

handle any more load. This proved that release agent reduces the interfacial adhesion in glass fiber reinforced epoxy composites.

The second sample is shown in Figure 6. This sample shows that fragmentations occurred in the third step of applied strain following by the collapse of the interface in the subsequent steps. At 0% matrix strain the fiber had no initial stress or strain while at 0.3% matrix strain the fiber showed elastic behavior following the elastic shear-lag model by Nairn (Yallee *et al.*, 1998; Stanford *et al.*, 2000). At 0.6% matrix strain, the fiber fractured into two fragments. Unlike the fiber without release agent applied (Sureeyatanapas *et al.*, 2009; Sureeyatanapas *et al.*, 2010) the small region around the fracture point showed interfacial failure



Figure 3. Mapping of COOH-SWNTs in the interfacial layer on glass fiber with release agent applied before fabrication in the epoxy using 0%, 0.3%, and 0.6% matrix strains.



Figure 4. Variation of ISS with distance along the fiber derived from specimen in Figure 2.



Figure 5. Optical micrographs of the SWNTs moving from the original position at high strain level of SWNTs sized on a glass fiber.



Figure 6. Mapping of COOH-SWNTs in the interfacial layer on glass fiber with release agent applied before fabrication in the epoxy using (a) 0%, 0.3%, and 0.6% matrix strains and (b) 0.9% matrix strain.

as can be seen from the SWNTs around the fracture points showing a maximum strain of 0.3%. Furthermore, it was found that the fully-bonded or elastic shear-lag model could be applied to the left fragment whereas the fully-debonded model of Kelly-Tyson (Kelly et al., 1965) could be applied to the right fragment as can be seen from the triangular fitting line. Finally at 0.9% matrix strain, the fully-debonded model was applied in certain areas along the fiber length as shown in the triangle fitting lines in Figure 6b. The interfacial failure occurred throughout the rest of the fiber length due to the release agent reducing the adhesion between the fiber and the matrix. The fiber could no longer reinforce or bear the load in the composite. This showed that higher strain applied could cause interfacial failure due to the fiber stress become higher than its ultimate bond strength (Berg et al., 1998) especially when the release agent was applied.

The variation of ISS with distance along the fiber derived from specimen in Figure 6 is shown in Figure 7. In this case, a complicated ISS distribution was obtained which were different in each strain level. In Figure 5a, at 0% and 0.3% matrix strains, a similar pattern was achieved as in the previous sample. Nonetheless, at 0.6% matrix strain the ISS distribution showed different patterns each side of the fracture points. The left line followed the elastic shear-lag model while the right line followed the fully-debonded model (Kelly *et al.*, 1965). In Figure 7b when the matrix strain equal to 0.9%, the ISS distribution was a straight line throughout

the fiber length representing full debonding. There was no more increase in the maximum ISS from that at 0.6% matrix strain which was 15 MPa. Therefore, increasing the matrix strain led to complete fiber/matrix interfacial failure.

4. Conclusions

This work has demonstrated that the strain profile at the fiber-matrix interface can be revealed by the technique used here. The fiber strain mapping of the model glass fibers without silane addition in the sizing layer and with release agent applied before being embedded in the matrix specimen was shown. It was found that the fiber strain profile was in good agreement with shear-lag theory (Sureeyatanapas et al., 2009) at the low matrix strain level during fragmentation of the glass fiber. At higher strain levels, the fiber/matrix interfacial failure was found to occur. The area around the fiber fractured points was debonded. The fully-debonded model proposed by Kelly-Tyson (Stanford et al., 2000) was used to fit the fiber strain at high strain level where the interfacial failure occurred. A maximum ISS of about 15 MPa was obtained. There was no more increase in the maximum ISS from 0.6% matrix strain. Increasing the matrix strain leads to fiber/matrix interfacial failure which causes less effective stress transfer in the composites. This proved that the release agent reduces the interfacial adhesion in glass fiber reinforced epoxy composites. The application of release agent at interface can also confirm the interfacial properties and deformation behavior of glass fiber/epoxy composites with the use of



Figure 7. Variation of ISS with distance along the fiber derived from specimen in Figure 4.

SWNTs as strain sensors. This also suggests that SWNTs can be applied to other composite systems as sensor application or used in modified materials.

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