JOURNAL OF MATERIALS SCIENCE **34** (1999) 105–110

Strain measurement for Raman-inactive substrates with PbO thin films using Raman Coating Method

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A new method of Raman spectroscopy to measure strain of Raman-inactive materials deposited with Raman-active thin films was proposed. This method is denoted as the Raman Coating Method. This is the application of Raman spectroscopy, in which thin films of PbO are deposited on the surface of resins and metals using physical vapor deposition (PVD) as the pretreatment to measure strain. The relation between peak shift of PbO thin films and tensile strain was experimentally examined. This relation was independent of the mechanical properties of materials on which PbO thin films were deposited. The residual stress in PbO thin films was also measured. The absolute values of residual stress in the films on resins were much greater than those on metals. As an application of the proposed method, the tensile strain in carbon fiber of carbon fiber reinforced plastics (CFRP) was measured by Raman spectroscopy. © *1999 Kluwer Academic Publishers*

1. Introduction

Carbon fiber reinforced plastics (CFRP) have been widely used recently in automobiles, aircrafts, and spacecrafts, because it is possible to reduce the weight of these vehicles. CFRP are inhomogeneous materials, consisting of fiber carbon reinforcement and matrix resin. Therefore, the value of phase stress differs within the material. There are few investigations in which the phase stress or phase strain in CFRP are precisely measured, because of the difficulty of experiments. It is important to measure phase stress to investigate fracture mechanisms of CFRP. Strain gauge analysis is not applicable to measure phase stress or phase strain of small regions.

Laser-Raman spectroscopy can be used for the measurements of phase stress or strain, because micro-Raman spectroscopy has excellent spatial resolution (0.3 nm $\sim$ 1000 nm) and precision in wave number. Because of these merits, laser-Raman spectroscopy has been widely used to determine local strain conditions of semi-conductive materials, although it was originally developed for the instrumental analysis in the field of chemistry. The wave number of Raman scatter is specific for each Raman-active material, therefore each Raman-active material has its own Raman peak. The position of the Raman peak of each Raman-active material varies due to change of conditions such as stress and temperature, therefore the strain can be measured by observing the peak shift. Raman spectroscopy is the general method of measurement for Raman-active materials [1–6]. However, not all materials are Raman-active. It is impossible to observe the Raman peak in the case of the materials that radiate fluorescence strongly. Moreover, it is also impossible to observe Raman-inactive materials such as metals; therefore, strain of these Raman-inactive materials cannot be measured using Raman spectroscopy.

There has been little research in which the strain in CFRP has been measured using Raman spectroscopy. Since CFRP radiate fluorescence, the Raman peak cannot be observed, therefore it is difficult to evaluate stress and strain conditions using Raman spectroscopy. On the other hand, as mentioned above, it is possible to observe the Raman peak of most of the semi-conductive materials and oxidized metals. Consequently, it is beneficial to coat thin films of Raman-active materials on Raman-inactive materials to be able to observe the Raman shift. The peak shift of the Raman-active thin film will be useful to evaluate strains.

One of the features of the measurements using Raman spectroscopy is that it is not necessary to process and prepare the specimens before measuring the Raman peak. The authors propose a method to measure strain of Raman-inactive materials using specimens with deposited Raman-active thin films in this paper. This method is denoted as the Raman Coating Method. It enables Raman-inactive materials to be observed by Raman spectroscopy. The thin films of PbO, a Raman-active material, were deposited on the surface of resins and metals using physical vapor deposition

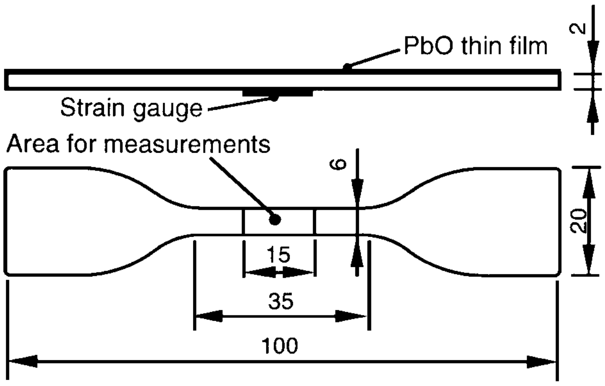

Figure 1 Dimensions of tensile specimen.

TABLE I Mechanical properties of substrates

Materials	CFRP[0] (#2500/ T300)	Epoxy resin (Ripoxy R802)	Epoxy resin (Epikote 828)	Aluminum alloy (A5052)	Stainless steel (SUS304)
Elastic modulus E GPa	102	3.07	3.64	76.9	252
Poisson's ratio ν	0.316	0.374	0.388	0.361	0.327

(PVD) as the pretreatment for the specimens to measure strain of resins and metals.

The relation between tensile strain and peak shift was obtained using vinyl ester resin with PbO thin films. Then the relation was examined using metals and bisphenoric resin deposited with PbO thin films to confirm that the relation has been independent of the deposited materials. The residual stress in PbO thin films was compared with that in PbO powder. Finally, on the basis of the relation between tensile strain and peak shift of PbO thin films, the tensile strain of carbon fibers of CFRP was measured by the proposed method.

2. Experimental procedure

The specimens with PbO thin films were prepared to determine the relation between peak shift of Raman spectra and strain. The materials of the specimens were vinyl ester epoxy resin (Ripoxy R802 Showa Highpolymer Co. Ltd.), bisphenoric epoxy resin (Epikote 828 Shell Chemicals), aluminum alloy (A5052), and stainless steel (SUS304), as shown in Table I. The mechanical properties of this vinyl ester epoxy resin were shown in Table I. The specimens were prepared at room temperature, cured for about 24 hours, then post-cured at 55 °C for two hours. On the surface of these specimens, PbO thin films were produced by resistance heating PVD. On another surface of the specimens, on which no PbO thin film was deposited, a strain gauge was adhered. Fig. 2 shows the tensile loading experimental apparatus. The tensile load was increased stepwise with about 35 N as shown in Fig. 3. The Raman spectra were measured with an argon ion laser of 514.5 nm. The spot size of the laser to measure strain was stopped down to about 1 μm by the object lens (100 times). The Raman spectra of the PbO thin films were measured at 8 points in the area for measurements on the specimens, shown in Fig. 1. The intensity of the laser was 100 mW, and the irradiated time was 150 seconds per measurement. The accuracy of the Raman spectroscope in wave number was 0.13 cm^{-1}. The electric vector of the incident beam was parallel to the loading direction. The experimental results of the Raman spectra near the top of the peaks were fitted into the Gaussian curve to determine the values of peak positions.

The tensile strain of carbon fiber of CFRP (#2500/T300 Toray Industry Inc.) was measured by Raman spectroscopy. The mechanical properties of CFRP are shown in Table I. Specimens of CFRP were made of a prepreg. The thickness of the CFRP specimens was 0.257 mm. The specimens were prepared in a vacuum bagging process at 130 °C for 2 hours. Then a PbO thin film was deposited on the surface of each CFRP specimen after curing. Tensile loading was applied to the fiber direction of the specimens. The experiments were conducted at room temperature (25 °C).

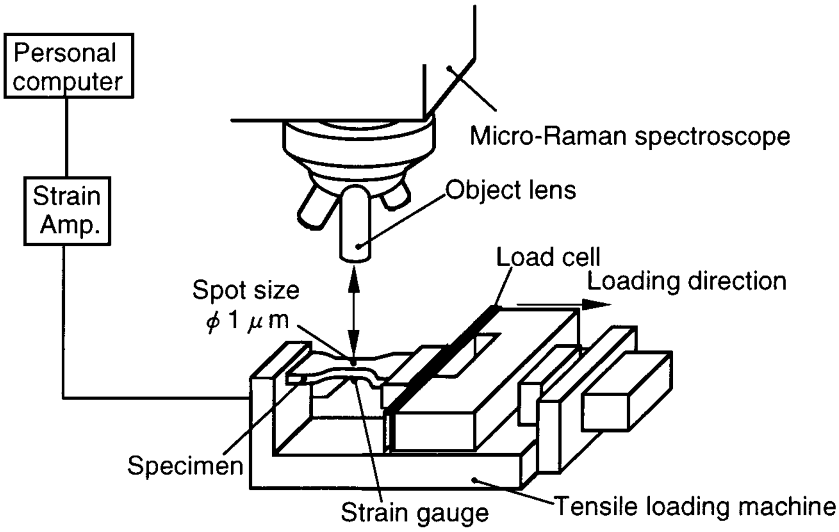

Figure 2 Schematic drawing of the experimental setup for Raman scattering measurements.

3. Experimental results and discussion

3.1. Characteristics of PbO thin film

The relation between peak shift $\Delta\omega$ and tensile strain ε measured by the strain gauge was obtained using the Raman peak observed at about 280 cm^{-1} as shown in Fig. 4 and Fig. 5.

Fig. 4 shows the results of the spectra of PbO powder and PbO thin film on the vinyl ester epoxy resin. The mean intensity of the Raman spectra of PbO thin films on the vinyl ester epoxy resin was 3.287 [Arb. Units], although the mean intensity of PbO powder was 131.3 [Arb. Units] measured under the same conditions. From this result, only 2.503% of the PbO powder was deposited as the film of PbO. The rest was deposited as a film of Pb and other oxidized Pb.

Fig. 5 presents the results of the spectra of PbO thin film for 0% and 0.4% of the tensile strain ε of epoxy resin, respectively. The peak positions of the Raman spectra were shifted to the lower wave number as the tensile strain increased. The mean peak position of the Raman spectra before loading occurred was $\omega_0 = 282.5\ cm^{-1}$. In addition, the full-width at half-maximum (FWHM) Γ_0 before loading was 16.00 cm^{-1}.

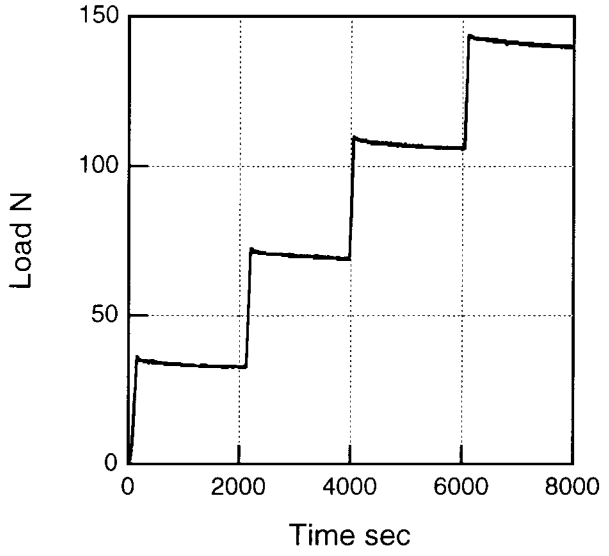

Figure 3 Loading history for tensile specimen.

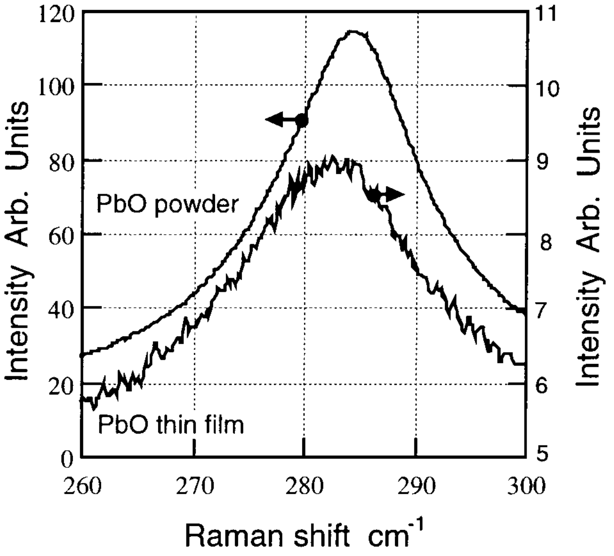

Figure 4 Raman spectra of PbO powder and thin films.

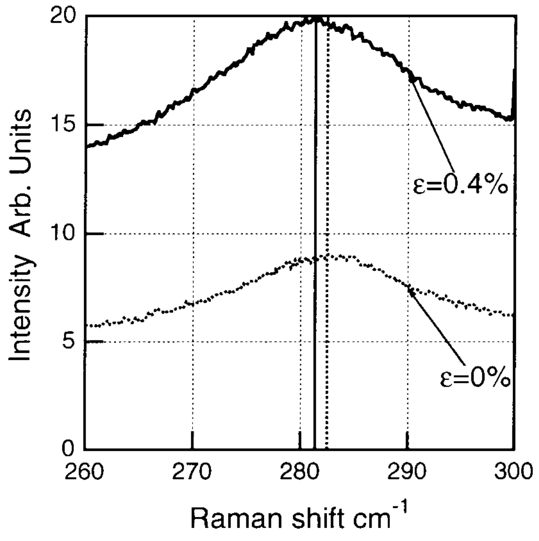

Figure 5 Raman spectra of PbO thin films.

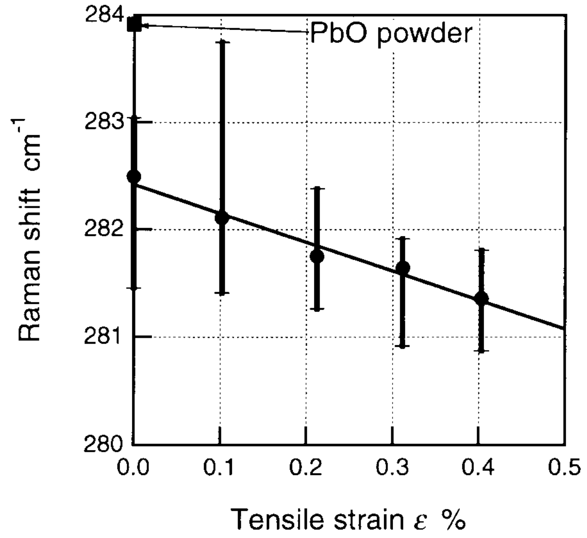

Figure 6 Plot of Raman shift vs. tensile strain.

Fig. 6 shows the relation between peak shift measured by Raman spectroscopy and tensile strain ε measured by the strain gauge. The mean values and the error bars are given in Fig. 6. The peak position of PbO powder is also shown in Fig. 6 for comparison. The value for PbO powder was measured 8 times. Obviously the Raman shift decreased linearly with the increase of tensile strain ε. The line was fitted by the least squares method. The peak shift $\Delta\omega$ could be represented by a function of the tensile strain ε measured by the strain gauge. The peak shift $\Delta\omega$ is expressed as

$$\Delta\omega = \omega_0 - \omega_\sigma \tag{1}$$

where ω_0 and ω_σ are the peak positions of PbO thin film before and after loading, respectively. The tensile strain ε of epoxy resin was related to the peak shift $\Delta\omega$ as the following equation.

$$\varepsilon\,(\%) = 3.705 \times 10^{-1}\Delta\omega\,(cm^{-1}) \tag{2}$$

Fig. 7 shows a plot of FWHM Γ of the Raman spectra measured experimentally as a function of tensile strain

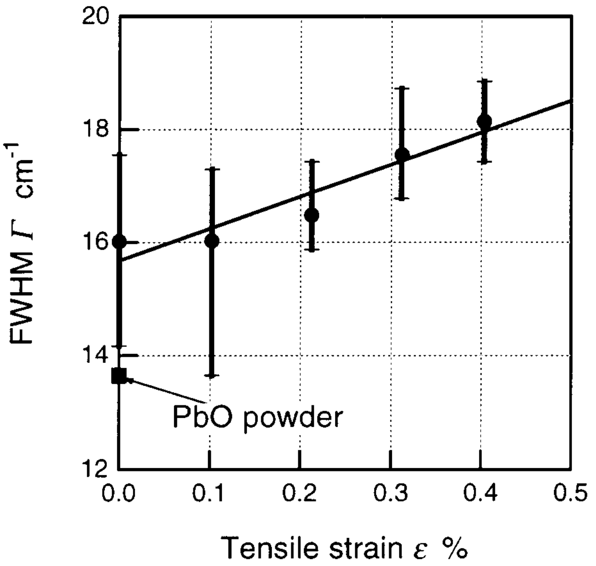

Figure 7 Plot of FWHM vs. tensile strain.

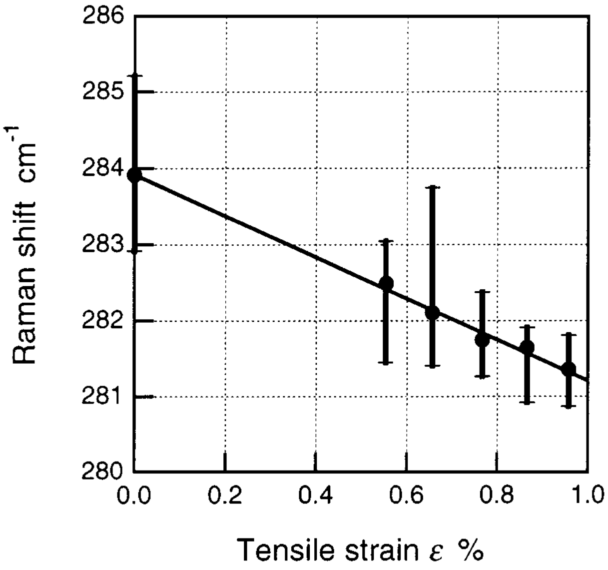

Figure 8 Plot of Raman shift vs. tensile strain.

ε of the epoxy resin measured by the strain gauge. The mean values and the error bars are also given in Fig. 7. The value of PbO powder is also presented for comparison. It can be seen that the values of FWHM Γ increase linearly with the increase in tensile strain ε of epoxy resin. This variation corresponds to inhomogeneous variation of strain distributions.

In general, residual stress is occurred in thin film deposited by PVD. In Fig. 6, the peak position of PbO powder is 283.9 cm^{-1}, although the peak position of PbO thin film before loading is 282.5 cm^{-1}. In addition, FWHM of PbO powder was 13.65 cm^{-1}, although FWHM of PbO thin film on epoxy resin without strain is 16.00 cm^{-1}. The peak positions of PbO thin films are different from those of PbO powder. Therefore the residual stress was evidently occurred, on the assumption that no stress is occurred in PbO powder. From Equation 2, the residual stress is calculated as the stress which occurs 0.555% tensile strain for the peak shift $\Delta\omega = 1.5$ cm^{-1}. When the strain in a PbO thin film is the same as that in the resin, the relation between peak shift and the tensile strain in PbO thin films can be obtained as Fig. 8. Similarly the relation between FWHM and the tensile strain in PbO thin films is also shown in Fig. 9. It can be seen that the plots of both Raman shift and FWHM are linearly varied. These figures show the existence of residual stress in PbO thin films after the deposition.

The peak shift is related to the function of the stress in vinyl ester epoxy resin measured by the load cell of tensile loading machine in Fig. 10. The average values and the error bars are also given in this figure. The stress was experimentally related to the peak shift $\Delta\omega$ by the following equation.

$$\sigma\,(\mathrm{MPa}) = 1.055 \times 10\Delta\omega\,(\mathrm{cm}^{-1}) \qquad (3)$$

3.2. Confirmation of characteristics of PbO thin film

Experiments were conducted to obtain that the relation of Equation 2 was independent of the deposited

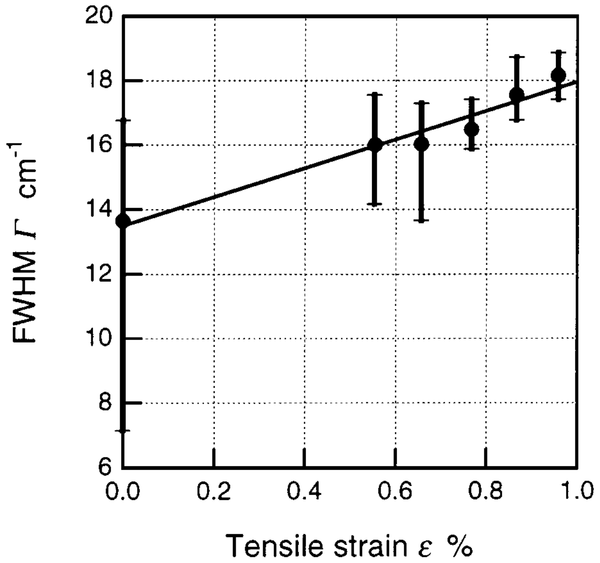

Figure 9 Plot of FWHM vs. tensile strain.

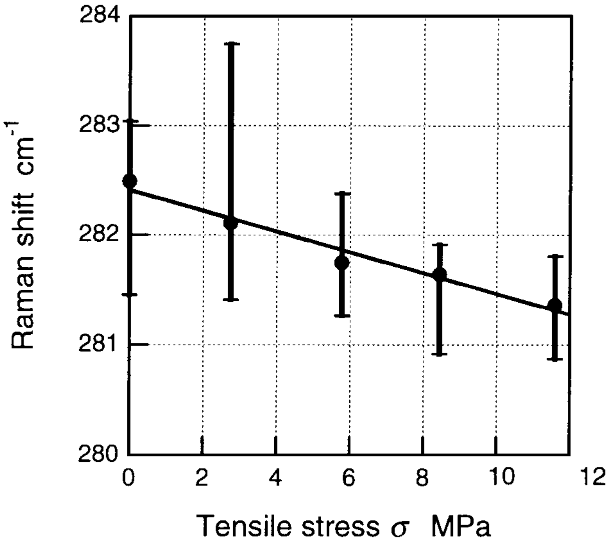

Figure 10 Plot of Raman shift vs. applied tensile stress.

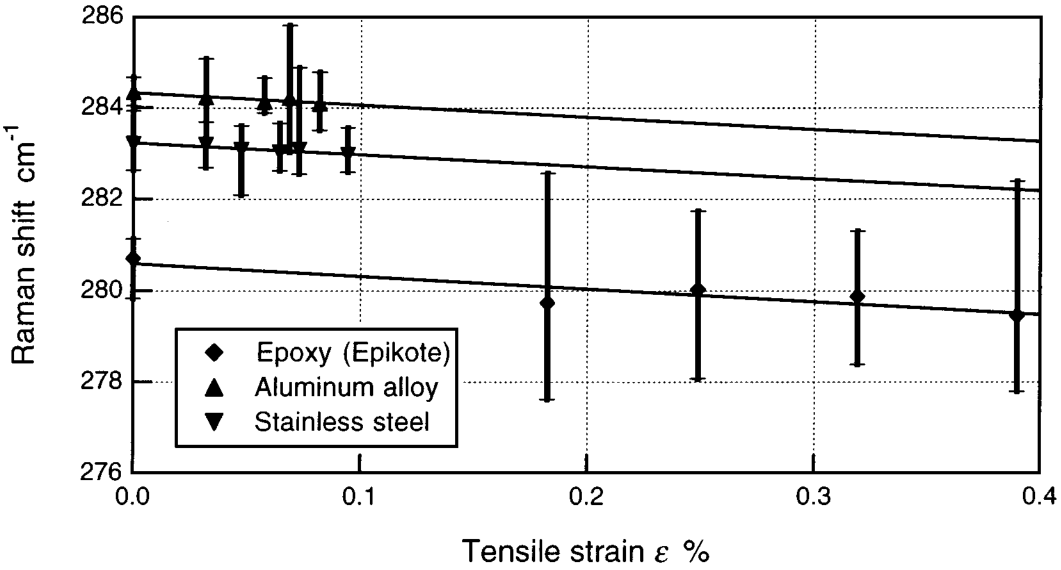

Figure 11 Plot of Raman shift vs. tensile strain for substrate.

materials. The substrates chosen were bisphenoric epoxy resin, aluminum alloy, and stainless steel. As can be seen in Table I, the mechanical properties are obviously different among these substrates.

Fig. 11 shows the relation between peak shift measured by Raman spectroscopy and tensile strain ε of each substrate measured by strain gauges. The measuring conditions were the same as the substrates of vinyl ester epoxy resin. The mean values and the error bars are also given in Fig. 11. From this figure, obviously, the peak shift decreased linearly with the increase in tensile strain ε for the substrates. As the line is fitted by the least squares method, the tensile strain ε was experimentally related to the peak shift $\Delta\omega$ by the following equation.

$$\varepsilon_{\mathrm{al}}(\%) = 3.730 \times 10^{-1}\Delta\omega_{\mathrm{al}}\ (\mathrm{cm}^{-1}) \quad (4)$$

$$\varepsilon_{\mathrm{sus}}(\%) = 3.823 \times 10^{-1}\Delta\omega_{\mathrm{sus}}\ (\mathrm{cm}^{-1}) \quad (5)$$

$$\varepsilon_{\mathrm{ep}}(\%) = 3.580 \times 10^{-1}\Delta\omega_{\mathrm{ep}}\ (\mathrm{cm}^{-1}) \quad (6)$$

where ε and $\Delta\omega$ are the tensile strain and peak shift, respectively, and subscripts of al, sus, and ep mean aluminum alloy, stainless steel, and bisphenoric epoxy resin, respectively. The gradients of the lines calculated by Equations 4 to 6 were almost the same. Therefore the relation between peak shift and tensile strain of substrates is independent of the substrates with PbO thin films.

The values of wave number of PbO thin films deposited on metals were approximately the same as those of PbO powder, though the wave number of PbO thin films deposited on resins were much smaller than that in the case of PbO powder. Therefore this implies that the absolute values of the residual stress of PbO thin films on resins are much larger than those on metals. The residual stress of PbO thin films is compressive when the substrate is the aluminum alloy, because the values of peak position is larger than 283.9 cm^{-1}. On the other hand the residual stress of thin films is tensile when the substrate is stainless steel.

3.3. Strain measurements of carbon fiber of CFRP

As seen in Fig. 6, the tensile strain in carbon fiber of CFRP was measured. Fig. 14 is the SEM micrograph of the surface of CFRP with deposited PbO thin film. It is possible to measure strain in the carbon fiber of CFRP, when PbO thin film can be produced on CFRP. As can be seen in Fig. 14, all of the carbon fibers of CFRP are parallel. In this measurement, the laser was applied to only carbon fiber selectively to measure the strain of the carbon fiber.

Fig. 12 is a stress-strain diagram of carbon fiber of CFRP obtained by Raman spectroscopy. The stress is calculated by dividing the tensile load by the cross-sectional area of the specimen. The strain ε was the mesoscopic value as the phase strain of carbon fiber measured by Raman spectroscopy. On the assumption that the strain in each phase is approximately the same, the elastic modulus of CFRP can be determined. From

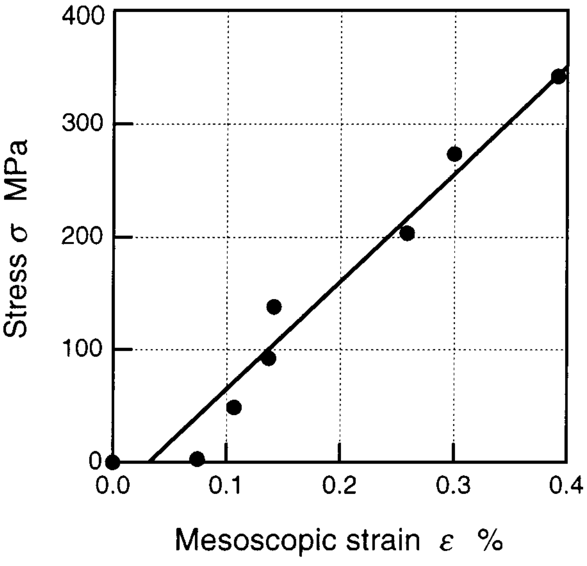

Figure 12 Stress-strain diagram of CFRP [0] measured with Raman spectroscope.

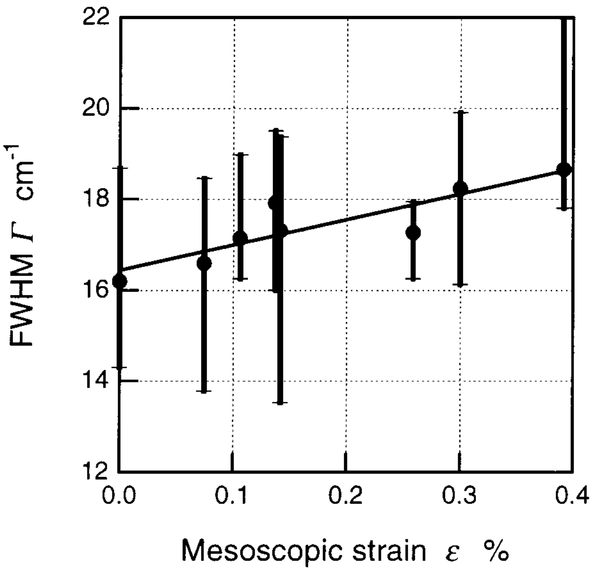

Figure 13 Plot of FWHM vs. tensile strain in case of CFRP[0]

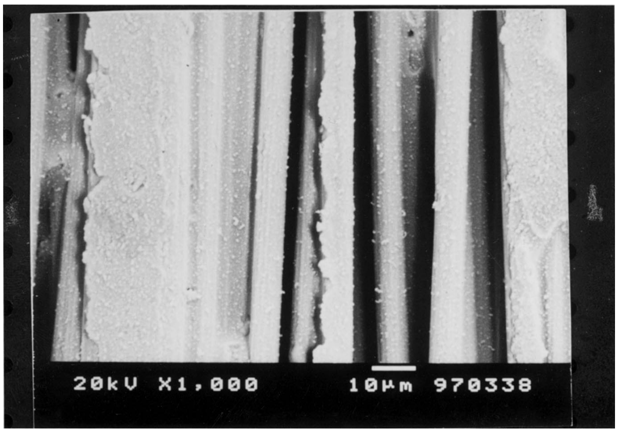

Figure 14 Surface of CFRP[0] with PbO thin film.

Fig. 14, the elastic modulus of CFRP was determined by the method of least squares as follows:

$$E_L = 95.5\ \text{(GPa)}.$$

Fig. 13 shows a plot of FWHM Γ of Raman spectra measured experimentally as a function of tensile strain ε calculated with Equation 2. The average values and the error bars are also given in Fig. 13. The values of FWHM Γ increased linearly with the increase in tensile strain ε of carbon fiber. Consequently Fig. 13 gives the confirmation of the result of Fig. 12. It is possible to measure strain selectively in the same phase of composites using Raman spectroscopy.

4. Conclusions

The Raman Coating Method was proposed to measure strain of Raman-inactive materials using deposited Raman-active thin films. The thin films of PbO were deposited on the surface of resins and metals using PVD as the pretreatment of Raman-inactive materials. The relation between the peak shift of Raman spectra and strain was experimentally determined. The strains of deposited materials were measured by tensile loading, and the results were compared with the strain measured by strain gauges.

(1) The characteristics of PbO thin films were obtained by Raman spectroscopy. The relations to peak shift and FWHM of deposited PbO thin films were linearly changed as strain. These relations were independent of the mechanical properties of the deposited materials.

(2) The absolute values of residual stress of PbO thin films deposited on resins were much greater than those deposited on metals. The residual stress of PbO thin films deposited on aluminum alloy was compressive, though the residual stresses of the films deposited on stainless steel and resins were tensile.

(3) The tensile strain in the carbon fiber in CFRP with PbO thin film was measured using Raman spectroscopy. The elastic modulus of CFRP was able to be determined from the stress-strain diagram measured by Raman spectroscopy.

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Received 1 December 1997
and accepted 15 July 1998