INTERFACIAL ASPECTS OF ELECTRODEPOSITED MULTI-FIBER REINFORCED COMPOSITES USING ELECTRO-MICROMECHANICAL TECHNIQUES AND ACOUSTIC EMISSION

Joung-Man Park[1], Sang-Il Lee[1], Young-Min Kim[1], Ki-Won Kim[2], and Dong-Jin Yoon[3]

[1] Dept. of Polymer Science & Engineering,
Regional Research Center for Aircraft Technology,
Gyeongsang National University, Chinju 660-701, Korea
[2] Dept. of Metallurgical Materials Engineering,
Gyeongsang National University, Chinju 660-701, Korea
[3] Failure Prevention Research Center,
Korea Research Institute of Standards and Science,
Taedok Science Town, Taejon 305-306, Korea

SUMMARY: Using electromechanical technique, various conductive carbon fibers and graphite and steel filaments/epoxy micro-composites were evaluated by measuring electrical resistivity to investigate the interfacial properties including the microfailure modes and inter-fiber distance effect with a aid of acoustic emission (AE). Micromechanical techniques, such as pull-out and fragmentation tests, and electrodeposition (ED) as a surface treatment method were combined. Testing micro-specimens were kept to be contacted electrically using silver paste with very thin copper wire on the conductive fibers. While tensile loading applied, the change of electrical resistivity was detected by fiber breakage and microfailure in micro-composites. In electro-pullout test, electrical resistivity was correlated to interfacial shear strength (IFSS) in a steel filament/epoxy composite by detecting maximum pull-out load and the increment mode of resistivity. Electro-micromechanical test was sensitive effectively to detect microfailure events and inter-fiber distance effect in graphite and carbon multi-fibers/epoxy composites. There were the correspondence between a fiber breakage and a sudden increment of electrical resistivity. AE was applied to correlate the microfailure occurrence from fiber break and matrix cracking and while testing for the untreated and ED treated specimens. By extending electro-micromechanical technique to 1-ply unidirectional carbon fiber/epoxy laminar under tensile load, electrical resistivity showed different microfailure trends for two narrow and wide specimens.

KEYWORDS: electro-micromechanical technique, electrical resistivity, electrodeposition (ED), multi-fiber composites, pull-out test, fragmentation test, interfacial shear strength (IFSS), acoustic emission (AE).

INTRODUCTION

Interfacial properties play an important role in controlling the mechanical performance in conductive carbon fiber/epoxy composites. Recently electromechanical pull-out test was reported in carbon or steel fibers/epoxy composites by measuring contact resistivity to provide the information on the interfacial adhesion and microfailure modes [1]. While tensile loading

was applied, electrical resistance (Ω) was detected by the decrement of filament diameter, frictional force of embedding fiber and filament breakage.
IFSS can be improved by an introduction of chemical functional groups via the oxidation of fiber surface, plasma or commercial coupling agent treatments. ED is a process that a polymeric film is deposited on a conductive fiber surface from a dispersion of colloidal ion in water with a charge opposite to that of the carbon fiber surface. By optimizing the treating process, a polymeric coating can be deposited with desired composition and thickness homogeneously to improve interfacial properties. The most frequently-used micromechanical techniques to measure IFSS include the single fiber pull-out test, the fragmentation test (or called as single-fiber-composites(SFC) test) etc [2, 3].
Due to the interfacial stress due to chemically induced contraction of the resin during the curing cycle and the matrix shrinkage based on the difference in the thermal expansion coefficient (TEC) between fiber and matrix a residual compressive stress can result in. A high residual stress can reduce the ultimate tensile strength and can cause the internal damage. For the microfailure detection and the interfacial properties, the electro-micromechanical technique can be use as a kind of nondestructive evaluation method economically because a conductive carbon fiber plays as a sensor role in itself, compared to relatively expensive fiber optics sensor.
Multi-carbon fiber, graphite and steel filament/epoxy composites were evaluated by measuring electrical resistivity with a aid of AE method to obtain the effect of the surface treatment by ED on the interfacial adhesion, and to characterize the microfailure modes and the inter-fiber distance effect while straining using the identical specimens under same load condition.

EXPERIMENTAL

Materials

Carbon fibers with diameter 8 and 18 μm, graphite filament with diameter 370 μm, and steel filament with diameter 280 μm were used as conductive reinforcing materials. Polybutadiene-maleic anhydride (PBMA) was used as a coupling agent to improve IFSS. Carbon fiber was coated in PBMA aqueous solution by ED. Epoxy resin based on diglycidyl ether of bisphenol A was used as matrix. Polyoxypropylene diamine (Jeffamine) was used as a curing agent to provide optimized flexibility for micro-tensile testing. 1-ply unidirectional carbon fiber/epoxy laminar (Hankook fiber Co., Korea) was also used for comparison.

Methodologies

Fiber Surface Treatment by ED: Fifty untreated carbon fibers with 8 μm diameter were fixed with regular distance apart in rectangular acrylic electrolytic frame. The frame size was 80 mm × 120 mm and acted as an anode in itself. The cathode was made of an aluminium plate bar with 2 cm width and 8 cm length. PBMA was diluted to the 0.5 wt.% concentration with deionized distilled water. After anode frame and cathode bar were immersed into 0.5 wt.% electrolyte solution, voltage of 1.1 V was supplied to both electrodes by power source. Typical locating time and applied voltage were 10 minutes and 1.1 V, respectively. After ED treated, electrodeposited carbon fibers were dried at room temperature without further thermal treatment, and some fiber were dried in the oven for comparison. The treated steel fiber was rubbed using very fine sandpaper to improve mechanical interlocking.

Preparation of Electromechanical Testing Specimens: Four types of specimens were used for electromechanical test. The first and second was single- or multi-fiber composites; the third was single fiber pull-out specimen; the fourth was 1-ply unidirectional specimen as shown in Fig. 1. After a pair of narrow copper wires was fixed transversely on dumbell-shaped silicon mold, conductive single or multi-fibers were laid down unidirectionally in the center of the same mold. The intersecting point between conductive fibers and copper wire was connected electrically by silver paste. The silver paste was used to keep electrical contact between narrow copper wire and conductive fiber. Then, epoxy mixture was poured into the silicon mold and precured at 80 ^{o}C for 2 hrs, and then postcured at 120^{o}C for 1 hr. 8 μm carbon fiber and 370 μm graphite fiber were used to prepare single- or multi-fiber composites for electro-micromechanical test. Dimension of dogbone-shaped specimen was as shown in Fig. 1(a). Distance between two electrical contact points was 32 mm. Especial space bar was used to control inter-fiber separation precisely in multi-fiber composites. Multi-fiber specimens with two kinds of inter-fiber distance were prepared. One is 1 time of fiber diameter, whereas another is 5 times. Single steel filament/epoxy composite was used for electro-pullout test. Embedding length and the distance between electrical inter-contacts of pull-out specimen were 5 mm and 4 mm, respectively. To extend the interfacial and electrical properties from micro-composites to real composites, 1-ply unidirectional carbon fibers reinforced epoxy laminar was applied. The dimensions of macro-specimen were 100 mm (length) x 0.2 mm (thickness) x 5 mm (width) as narrow specimen and 100 mm (length) x 0.2 mm (thickness) x 10 mm (width) as wider specimen, respectively. Distance between two electrical contact points was 75 mm.

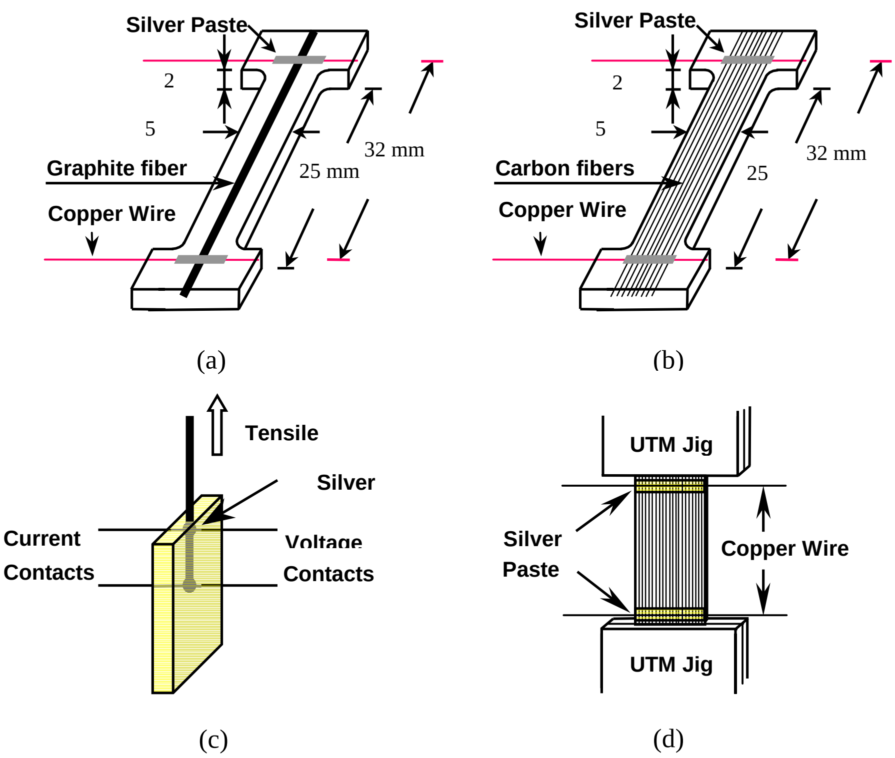


Fig. 1: Dimensions of four testing specimens for elecromechanical test.

IFSS Measurements while Electromechnical Test: After electromechanical test was done, IFSS parameters were measured under polarized-light microscopy. IFSS was determined using well-known Kelly-Tyson equation. The relationship among critical fragment length l_c, fiber strength σ_f, and fiber diameter d are as follows: $\tau = (\sigma_f\, d)/(2l_c)$. IFSS, τ_i by single fiber electro-pullout test was calculated from the measured pull-out force using following equation: $\tau_i = F_d /(\pi D_f L)$, where D_f and L are fiber diameter and fiber embedded length in the resin, respectively.

Determination of Electrical Resistivity using Electromechanical techniques: The electrical resistance between two voltage contacts was measured using a HP34401A digital multimeter and four probes method, as illustrated in Fig. 2. Mechanical propeties measurement were carried out using Universal Testing Machine (Lloyd instruments Ltd) at a cross-head speed of 0.1 mm/min, and 10 KN load cell. After testing specimen was fixed, and specimen and multimeter were connected electrically, tensile load was applied continuously with monitoring the electrical resistance of the specimen simultaneously. Electrical resistivity is given by the product of electrical resistance, cross-sectional area of conductive fiber (A), and length of fiber contacting to copper wire (L_{ec}). The relationship between electrical resistivity (ρ) and resistance (R) is as follows: $\rho = (A / L_{ec}) \times R$.

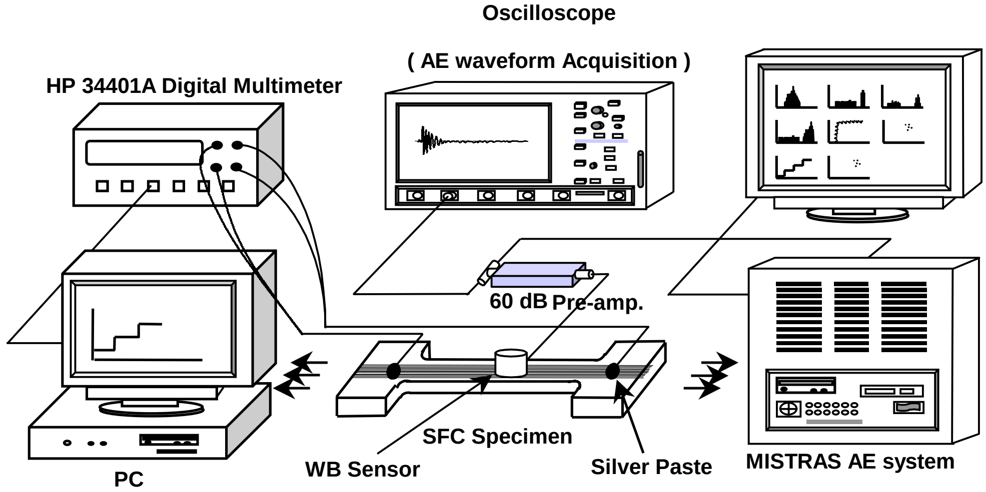


Fig. 2: Combined system with digital multi-meter and AE using micro-specimen.

Measurement of AE: Testing specimen was placed on the specially designed desk-top tensile machine for applying unidirectional tensile force. AE sensor was attached to the center of the testing specimen using a vacuum grease couplant. After AE test was done, the number of fragmentation of fiber and the microfailure in the testing specimen were observed via the polaroid microscopy. AE signals were detected by a wideband type sensor (model WD by PAC) with maximum sensitivity of –60 dB (ref. 1V/ubar) at 550 kHz. The sensor output was amplified by 60 dB at preamplifier and passed through a band-pass filter with a range of 100 kHz to 1200 kHz. Then the signal was fed into an AE signal processing unit. MISTRAS 2001 system, where AE parameters were extracted. The threshold level was set to 30 dB. The output from preamplifier was also connected to the digital oscilloscope (LeCroy 9354A), where each AE signal was recorded analyzed. Typical AE parameters such as hit rate, peak amplitude, and event duration were investigated for the time and the distribution analysis.

RESULTS AND DISCUSSION

Improved Interfacial Properties by ED Treatment: Table 1 shows the comparison of IFSS in carbon fiber/epoxy composites depending on the various surface treatment on the carbon fiber. In case of electrodeposited PBMA, the improvement in IFSS exhibited the highest. It may be due to the effectively-bonded coupling layer than the others by transferring stress efficiently via matrix into fiber. For aging treatment case, however, IFSS decreases abruptly, because active functional groups were degenerated or reduced by thermal treatment.

Table 1: IFSS of carbon fiber/epoxy composites depending on the treatment conditions

Condition	No. of Breakage (EA)	Ave. Fragment Length (μm)	IFSS (MPa)
Untreated	27	650	27.3
Dipping PBMA	38	500	37.5
Electrodeposited PBMA	59	330	60.0
Aging*	30	628	29.3

*Aging condition is at 80 °C for 30 min.

Interfacial Consideration by Electromechanical Technique: Table 2 shows the intrinsical values of electrical resistance and resistivity for four conductive fibers and filaments. Electrical resistance and resistivity of carbon fiber are larger than steel filament because of intrinsic properties of materials. Although electrical resistance are depending upon the diameter, electrical resistivity was exhibited differing values for two diameter carbon fibers. It may be because of different materials properties based on raw source materials while manufacturing.

Table 2: Intrinsical electrical resistance and resistivity for four conductive fibers and filaments at measured gauge length (32 mm) between inter-contacting points

Fiber	Diameter (μm)	No. of Sample (EA)	Electrical Resistance (Ω)	Electrical Resistivity ($\Omega.cm$) $\times 10^{-4}$
Graphite filament	370	7	1.60 (0.04)	5.37 (0.14)*
Steel filament	280	8	0.57 (0.07)	1.09 (0.14)
Carbon fiber	18	7	1.57×10^{3} (120)	12.5 (1.0)
Carbon fiber	8	8	1.186×10^{4} (570)	18.6 (0.9)

*Standard deviation

Fig. 3 shows typical plots of stress-strain curve and simultaneous plots of electrical resistivity *versus* time using electro-pullout test. Because the interfacial weak adhesion in the untreated steel fiber/epoxy specimen, the untreated steel fiber was pulled-out suddenly, then electrical resistivity increased infinitely. On the other hand, due to the improved interfacial adhesion of the treated steel fiber/epoxy composite by mechanical interlocking, the treated fiber was not pulled-out abruptly from matrix. When loading stress reached at the maximum, fiber pulling-out was observed first, but electrical resistivity increased only to small level initially. Based on the occurrence by the interfacial friction, electrical resistivity increased gradually and then finally became infinite.

Comparisons of stress *versus* strain curve and resistivity *versus* time between single 8 μm carbon fiber/epoxy and single 18 μm carbon fibers/epoxy specimens are shown in Fig. 4. The different trends were shown by observing the increasing modes of electrical resistivity depending on carbon fiber diameter by electro-micromechanical test. When a fiber is broken, electrical resistivity increased infinitely for both two specimens. However, a very abrupt change of electrical resitivity caused by a fiber fracture was detected in 8 μm carbon fiber reinforced epoxy specimen. It is considered because the 8 μm carbon fiber has higher resistivity and a sudden diconnection of thin diameter fiber compared to 18 μm carbon case.

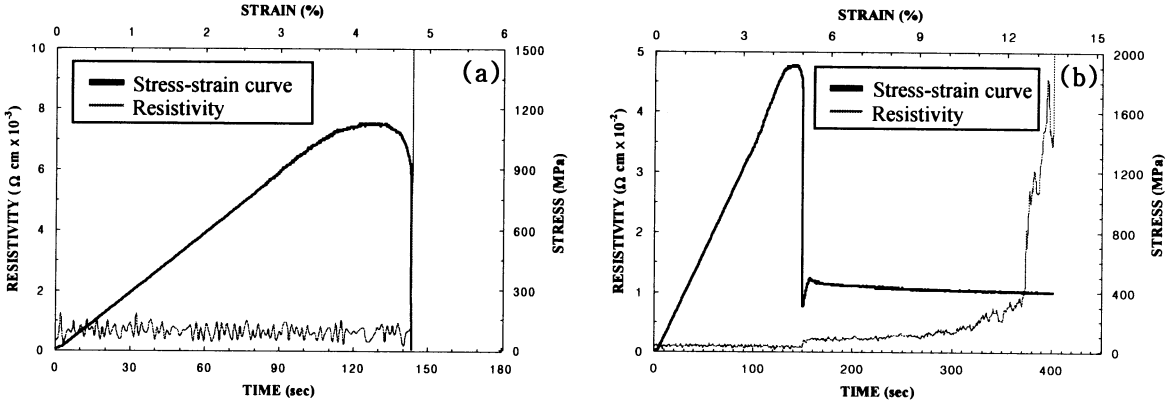


Fig. 3: Comparison of electrical resistivity and stress between (a) the untreated and (b) the treated single steel filament/epoxy composites using electro-pull out test.

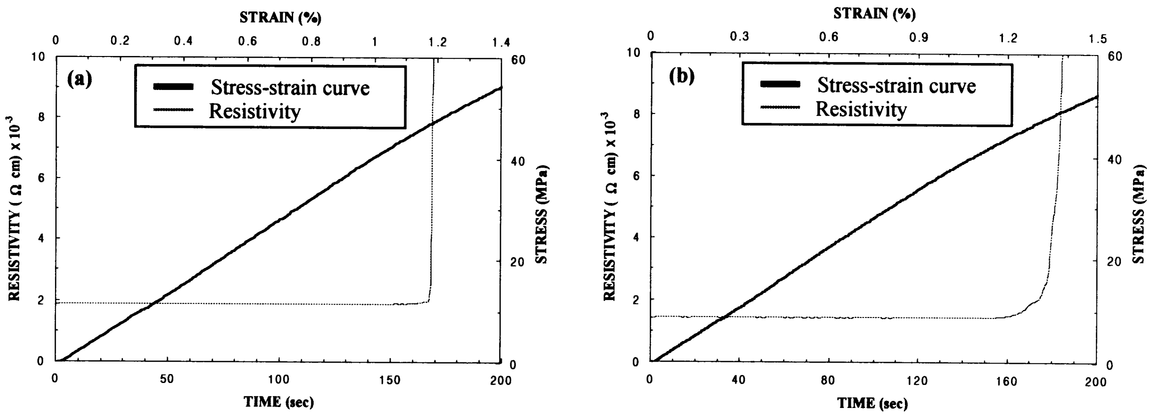


Fig. 4: Electrical resistivity in (a) 8 μm and (b) 18 μm carbon multi-fiber composites.

In Fig. 5, electrical resistivity and stress in single 370 μm graphite fiber/epoxy specimen using electro-micromechanical test. Behaviour of electrical resistivity in single graphite reinforced specimen showed the different trend compared to those of the 8 and 18 μm carbon fiber reinforced specimens. Generally electrical resistivity increased steadily and then rapidly increased, and finally become infinite at the end. Up to a certain level of low strain randomly-fractured fiber failure might affect dominately on the steady increase of the resistivity.

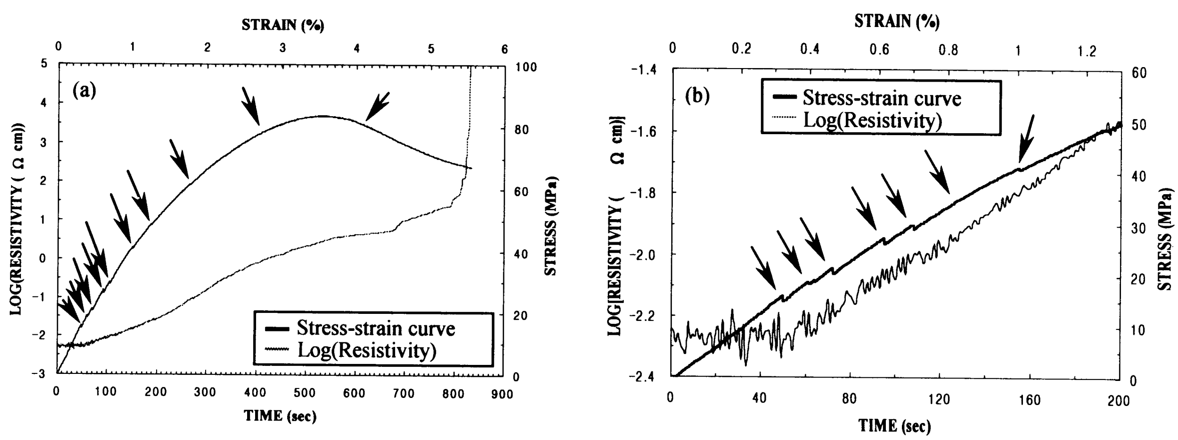
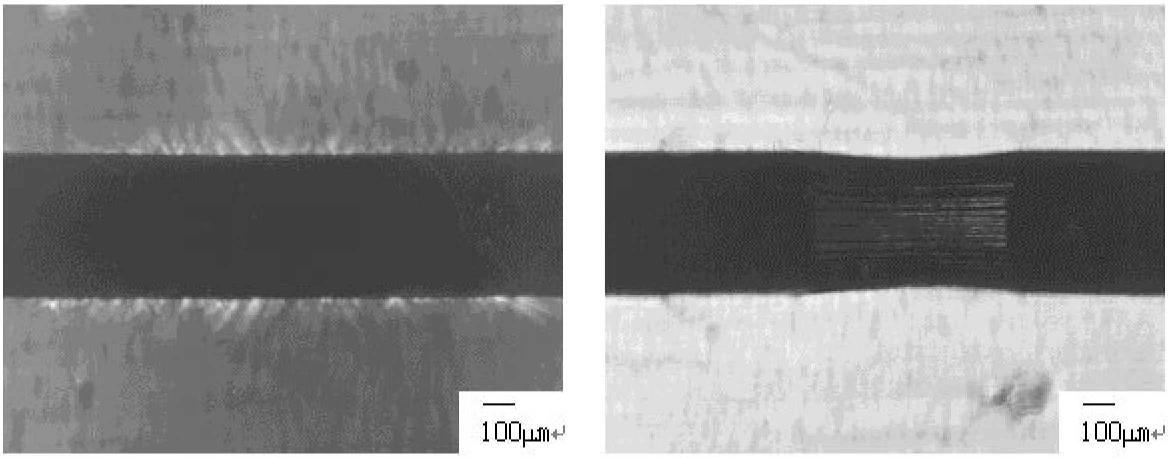


Fig. 5: Logarithmic resistivity and stress depending on testing time and strain in single

graphite fiber/epoxy composite: (a) total time range; (b) initial time range.

The fracture modes of graphite fiber in electro-microspecimen are shown in Fig. 6. At initial 0.3 % strain there is still partial contact intimately in the in Fig. (a), whereas at 2 % strain relatively large gap between broken fiber fragment was observed as a void. Such a larger gap result in the complete disconnection of electrical contact to cause the rapid increase of electrical resistance at high strain level. At initial stage the abrupt decrease of stress curve and a roughly linear increase of resistivity were observed clearly as fiber fracture occurred.



(a) (b)

Fig. 6: Typical failure mode of single graphite fiber/epoxy specimens while testing:
(a) at 0.3 % strain; (b) at 2.0 % strain.

Fig. 7 shows the change of electrical resistivity and stress as a function of the testing time and strain in (a) narrow and (b) wide multi-fiber composite specimens. The narrow system was made of 8 μm carbon multi-fibers using 1 time inter-fiber spacing bar, whereas the wide system was prepared with 5 times inter-fiber distance. In narrow fiber space specimen, about two groups were well separated as the series of successive fiber fracture as shown in Fig. 7 (a) due to the impact effect from the fracture energy of a fiber break to neighboring fiber. Characteristic fiber fracture modes exhibited and many fibers were broken in a series around neighboring fibers. In the wider inter-fiber composite rather irregular and random increments of resistance were appeared at the weakest point among multi-fibers as shown in Fig. 7 (b).

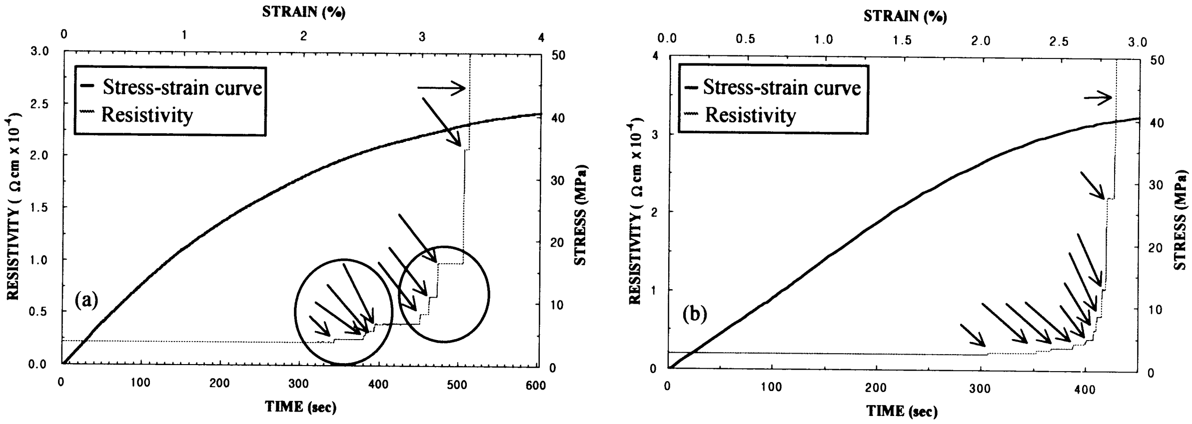


Fig. 7: Comparison of electrical resistivity with different inter-fiber spacing in
(a) narrow-; and (b) wider multi-carbon fiber/epoxy composites.

Fig. 8 shows fiber failure modes of multi-carbon fiber/composites with wide inter-fiber spacing. Breaking position of the individual fiber exhibited rather random or irregular.

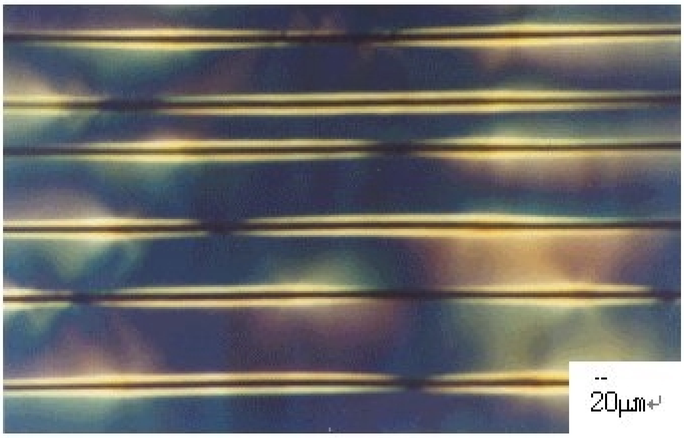


Fig.8: Photograph of random fiber break of multi-carbon fiber composite via polarized-light microscopy.

Fig. 9 shows comparison of logarithmic resistivity and stress in the triple 370 μm graphite fibers/epoxy specimens with (a) 1 time inter-fiber spacing and (b) 5 times inter-fiber spacing. Electrical resistivity increased steadily for both cases. Number of fiber fracture was 17 EA in narrow spacing gap speciemen, whereas the number of fiber break was 29 EA in wide spacing gap specimen, respectively, because of the fracture energy afffects on the nearly adjacent fibers. The wider inter-fiber distance, the higher IFSS from Kelly-Tyson equation.

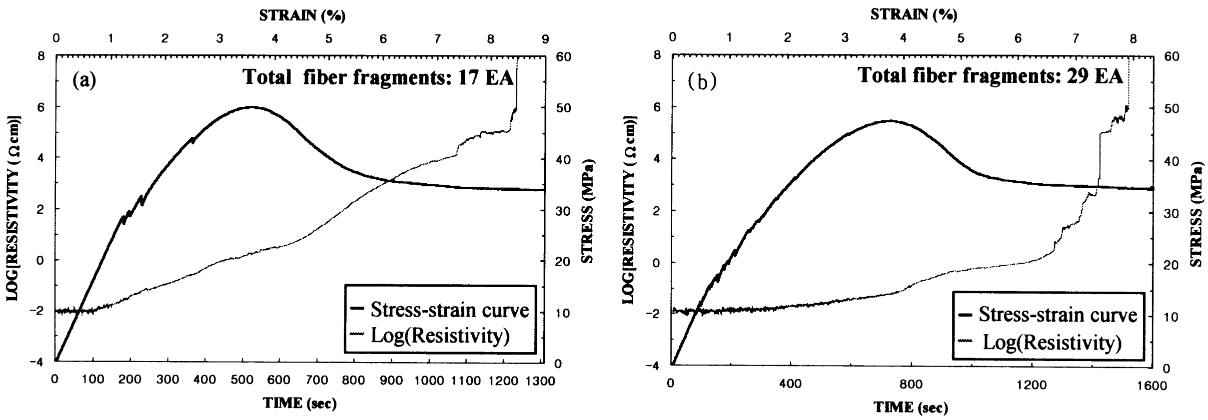


Fig. 9: A comparison of logarithmic electrical resistivity depending on (a) 1 time and (b) 5 times inter-fiber spacing in the triple-graphite fiber specimens.

Fig. 10 shows plots of stress *versus* strain and simultaneous plots of elecrical resistivity *versus* time for (a) the untreated and (b) the ED treated multi-fiber composites with combined of AE test. Changes of electrical resistivity was accordance with detected AE signals in both the untreated and the ED specimens. The AE event number of high energy group in Fig. 10 (b) were more than the number in Fig. 10 (a). It is considered because of the improved IFSS by electrodeposited coupling agent. Generally more matrix cracking events occurred in ED treated composites compared to the untreated. It may be because the microfailure of interlayer may result in relatively lower AE events.

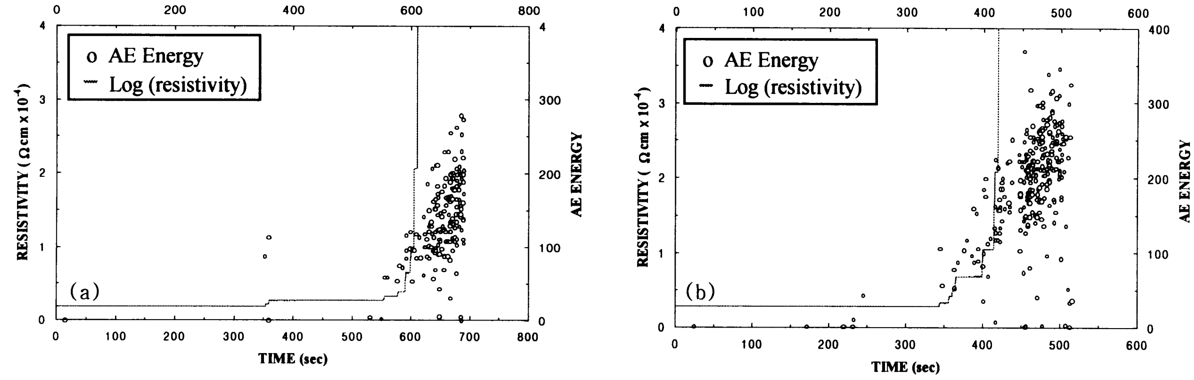


Fig. 10: AE energy and electrical resistivity by surface treatment in the 8 μm carbon multi-fiber/epoxy composites: (a) the untreated; (b) the ED treated multi-fibers.

Fig. 11 shows AE energy distribution and resistivity *versus* testing time for (a) 18 μm multi-carbon fibers/epoxy and (b) 370 μm single graphite/epoxy composites. In Fig. 11(a), electrical resistivity in the untreated specimen was reached early to the infinite than the other fiber specimens. It is considered due to brittle properties of the untreated 18 μm carbon fiber in itself. Generally as fiber diameter increases, AE energy range from fiber fracture also increases rapidly. Fig. 11 (b) shows logarithmic electrical resistivity and AE energy with testing time in 370 μm single graphite fiber/epoxy specimen. Fiber fracture occurrence in the specimen was identified while AE testing acoustically as well as in terms of AE events.

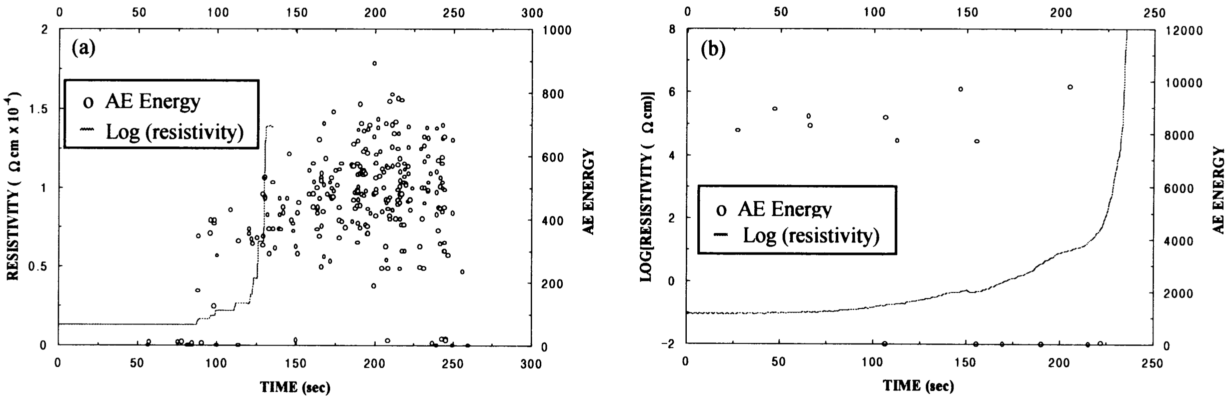


Fig. 11: Comparison of AE energy and electrical resistivity for two differing diameter fibers: (a) 18 μm multi-carbon fibers; (b) 370 μm single graphite fiber.

Fig. 12 shows the correlation of electrical resistance with stress depending on the time and strain using electro-macromechanical test in 1-ply unidirectional carbon fibers laminar specimen by extending to real composite. After maximum stress, a narrow ply specimen exhibited relatively-sudden catastrophic failure mode and rapid resistance increase in Fig. 12(a), whereas a wide ply specimen occurred the stepwise failure mode in Fig. 12(b). It can be considered that microfailure modes and interfacial aspects using micro-composite specimens can also be extended and correlated well with macro-composite specimens.

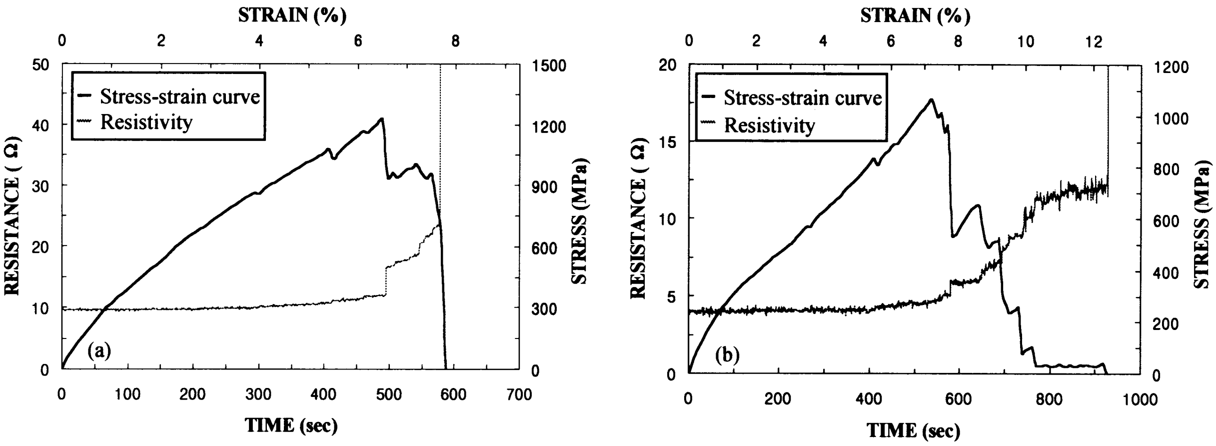


Fig. 12: Changes of electrical resistance and stress of 1-ply unidirectional laminar specimens with (a) 5 mm and (b) 10 mm width.

CONCLUSIONS

Using electro-micromechanical techniques, multi-carbon fibers, graphite and steel filaments/epoxy micro-composites were evaluated by measuring electrical resistivity combined with AE to know the effect of the surface treatment by ED, and to characterize the microfailure modes and the inter-fiber distance effect. PBMA electrodeposited carbon fiber exhibited significantly higher IFSS than those of the untreated owing to active chemical or functional groups and improved coating layer on the fiber surface. For electro-pullout test, interfacial frictional effect in the steel filament specimens was observed by different changing modes of electrical resistivity due to the improved interfacial adhesion. Electrical resistivity and resistance increased by broken fibers in multi-fiber specimens and real laminar composites. Electrical resistivity increased stepwise in carbon multi-fiber specimens, whereas it increased linearly in graphite multi-fiber specimens. Electrical resistivity were separated into two or three groups in regular multi-fiber composites with narrow inter-fiber spacing. It is considered because the fracture energy caused by a fiber break affected adjacent fibers. The results obtained from AE method are consistent reasonably well with experimental data measured by electro-micromechanical technique. Electro-micromechanical technique connected with AE technique can be useful in evaluating nondestructively the interfacial properties of conductive fiber reinforced composites including the nontransparent specimens.

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