STUDY ON FABRICATION AND ELECTRIC PROPERTY OF B-STAGE RESIN FILMS CONTAINING CARBON NANAO MATERIALS

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1 Introduction

Recently, composite materials reinforced with carbon nano materials have been investigated for a variety of applications based on their unique electrical, mechanical and thermal properties. In the particular case of carbon composite resin film, it is useful for electrical devices such as FED (field emission display), transparent electrode, EMI (electromagnetic interference), ESD (electrostatic discharge), capacitors [1-3].

There are many processes to manufacture carbon composite resin films which are tape casting, solvent casting, spin casting, slip casting. Tape casting method as a continuous process is very useful for preparing thin films. It has been widely used to produce polymer resin film and ceramic film [4-6].

Tape casting method is uni-direction process. The fibrous fillers are directionally aligned due to shear force in the slurry during the fabrication of fibrous-filler-reinforced film. So, the composite film shows orthotropic properties according to the casting and its transverse direction. This situation was also investigated in previous studies on the property of aligned-ceramic-reinforced films [5, 6].

Orthotropic feature of carbon composite resin film is expected to affect the electrical, mechanical property. Andrews *et al.* [4] studied that thin films of Mutli-walled CNT-filled composites were oriented purposely using spin casting methods and were observed electrical, mechanical property.

The orientation of carbon nano material in tape casting process is expected to be dependent on the combination aspect ratio of the material and film casting heights. In this study, carbon composite resin films were fabricated by tape casting method. The influences of the film thickness and combination of carbon nano materials on the electric property were investigated through the measurements of DC and AC electric field. Electric property in the in-plane direction was measured in electromagnetic wave of TEM mode in X-band. The electrical conductivity of films was observed along the casting and transverse directions. The orthogonality of the electric property was verified with the investigation of the SEM images of the fractured cross sections of the films.

2 Experiment

2.1 Materials

Table 1 shows the carbon nano materials used in this study. Epoxy resin system used combination of several resins from Kukdo Chemial Co.

Table 1 Carbon nano materials used experimental

Material	Company	Appearance	Diameter [nm]	Length [μm]
CNT	Hanhwa nanotech	Tube	10-15	10-20
Pyrograf	Applied Science	Fiber	150	30-100
VGCF	Showa-Denko	Fiber	150	10-20
CB	Ketjenblack	Pellets	-	-

2.2 Fabrication of composite films

Carbon nano materials were added to polymer resin with certain content (Table 2). After pre-mixing, the mixture was dispersed using a 3-roll mill. The processing was performed 5 times repeatedly at 10 μm for the gap distance between the rolls and the roll rotation speed was set to 200 RPM. Carbon composite films of various casting heights (0.1, 0.2, 0.3mm) were fabricated using a comma roll-type film casting device equipped with micrometers and cured in an oven for 120^{o}C for 150 min. Fig. 1 shows the scene of the tape casting and the notation of the directions. D-1 and D-2 are the casting and transverse directions respectively.

Table 2 Samples and their filler contents

Sample No.	Filler 1	Filler 2
1	CNT, 2wt%	CNT, 2wt%
2	CNT, 2wt%	Pyrograf, 2wt%
3	CNT, 2wt%	VGCF, 2wt%
4	CNT, 2wt%	CB, 2wt%

Fig. 1 Scene of tape casting and notation of the directions

2.3 Measurement of AC electric property

AC electric property, so called complex permittivity, is simply expressed by $\varepsilon = \varepsilon' - j\varepsilon''$, where ε' is dielectric constant and ε'' is lossy term that is related with the AC electric conductivity of the material written as $\varepsilon'' = \omega\varepsilon_o\sigma_{ac}$ where ω is angular speed for frequency f, ε_o is a dielectric constant for vacuum (or air) and σ_{ac} is the electric conductivity of the composites. In order to measure the complex permittivity in X-band (8.2~12.4GHz), Agilent N5230A and HVS free space measurement system was used as shown in Fig. 2 [7].

The nanocomposite resin films were measured positioning these in the parallel and transverse directions of the unidirectional electric.

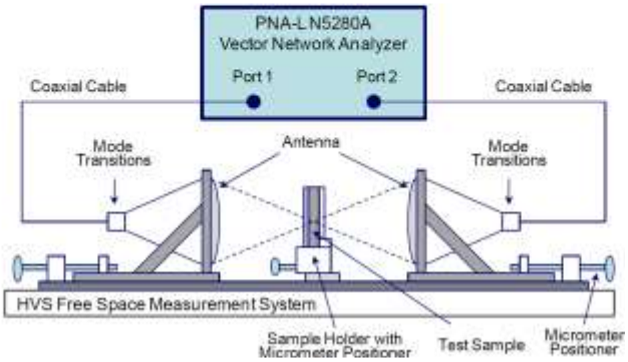


Fig. 2 HVS free space measurement system

2.4 Measurement of DC electric conductivity

DC electric conductivity of carbon composite film was measured to observe the effect of film thickness on the orthogonality of the electric property. The specimen dimensions are 10*100mm. The resistance was measured by the 2-probe resistance method using a True RMS multi-meter (FLUKE). The electric conductivity was calculated from the measured resistance as below.

$$\sigma = 1/\rho = l/AR$$

(σ : electric conductivity, ρ : electric resistivity, R : resistance, A : cross sectional area of a specimen, ℓ : length of a specimen)

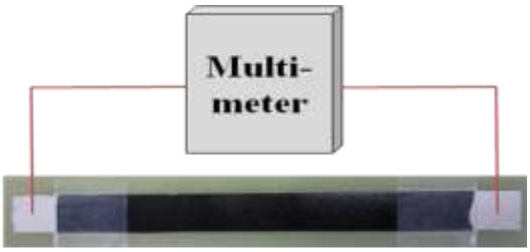


Fig. 3 Configuration of the specimen for the resistance measurement

3 Result and Discussion

3.1 Fracture surface of nanocomposite resin films

Microscopic configuration of film fracture surfaces were observed by using a SEM (JEOL, JSM-5800) to verify the directional distribution of dispersed carbon nano materials. Fig. 4 (a, b) shows that the film is well made with good dispersion of carbon nano materials. The images of the fracture surfaces in D-1 and D-2 directions were compared in each film including Fig. 4 (c-1) and (c-2) of CNT 4wt%, (d-1) and (d-2) of CNT+Pyrograf 4wt%, (e-1) and (e-2) of CNT+VGCF 4wt% and (f-1) and (f-2) of CNT+CB 4wt%. The fiber diameter of Prograf and VGCF are so much bigger than CNT that Prograf, VGCF in the composite films were observed to be well aligned along the casting direction. Along the transverse direction, holes of pull-out fibers can be observed.

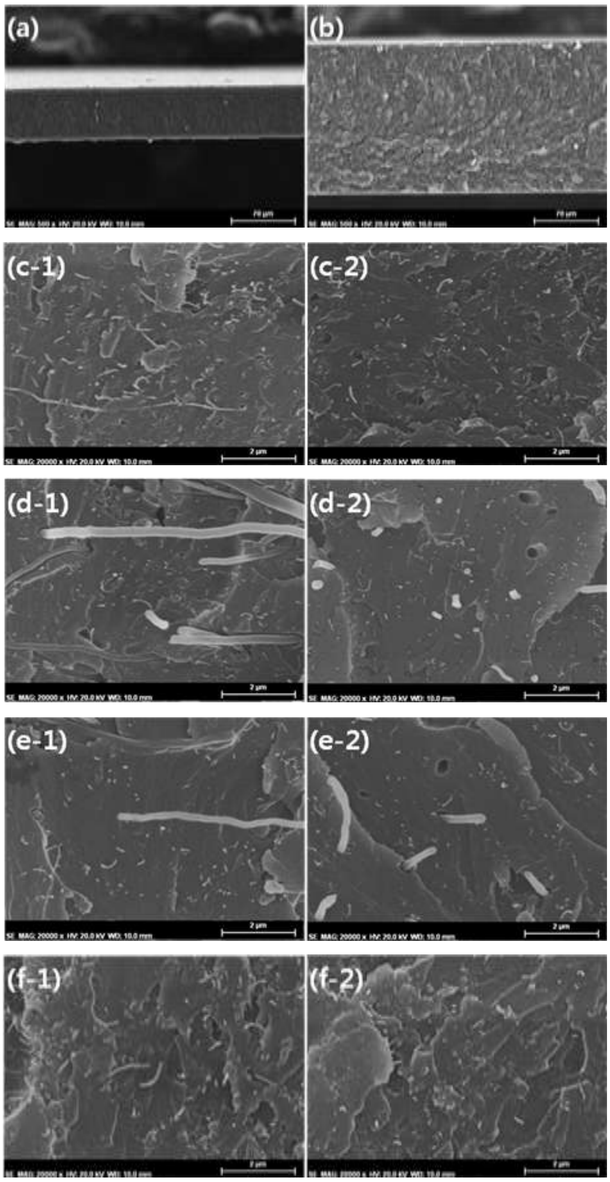


Fig. 4 SEM image of film fracture surface (a, b); (c) CNT, (d) CNT+Pyrograf, (e) CNT+VGCF, (f) CNT+CB; #-1 (casting direction), #-2 (transverse direction)

3.2 AC electric properties of composite films

Fig. 5 shows dielectric property of the CNT 4wt% film in 8.2~12.4GHz frequency in D-1 and D-2 directions representatively. In all frequency range, the electric properties (ε', ε'') are significantly different according to the measurement direction, which is due to alignment of carbon nano materials during the casting process. The measured thickness of every film is almost half of its original casting heights. Table 3 shows the measured film thickness and complex permittivity at 10GHz of the films.

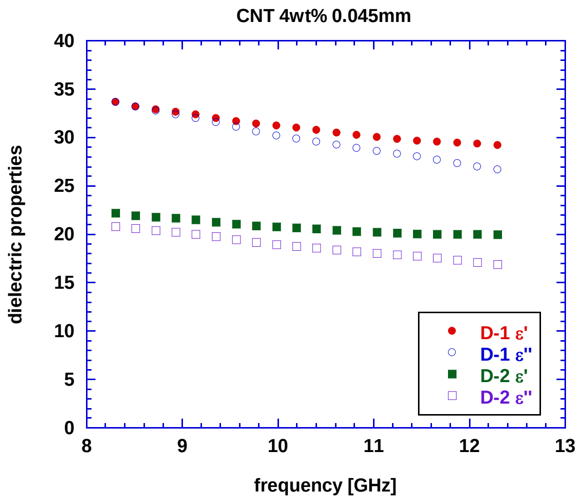


Fig. 5 Complex permittivity of the CNT 4wt% film for 8.2-12.4 GHz (casting height is 0.1 mm)

Table 3 Measured film thickness and complex permittivity at 10 GHz

Sample No.	Thickness [mm]	D-1 ε'	D-1 ε''	D-2 ε'	D-2 ε''
1 (CNT)	0.045	32.31	29.83	21.69	18.68
	0.098	28.01	34.77	19.04	22.70
	0.155	25.82	32.90	18.15	21.92
2 (CNT+ Pyrograf)	0.049	36.94	16.40	19.94	8.77
	0.100	36.05	17.57	18.76	8.99
	0.172	31.57	16.76	17.15	8.99
3 (CNT+ VGCF)	0.042	22.77	13.52	11.84	7.97
	0.094	21.94	15.15	12.18	9.10
	0.165	18.71	13.89	11.52	8.75
4 (CNT+ CB)	0.044	17.65	12.69	11.88	8.58
	0.094	16.77	14.95	12.00	10.37
	0.152	15.56	14.30	11.50	10.10

In comparison of ε'' values in D-1 direction, CNT films are the highest among the 4 samples, which is due to the high electric conductivity of CNT. But, in comparison of ε' values in D-1 direction, CNT+Pyrograf films are the highest, which is different from the case of ε''. It is estimated to be from the great length of the Pyrograf [8].

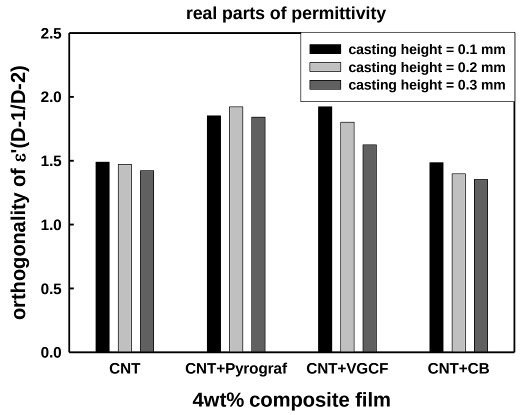
The order in ε' and ε'' in D-1 direction can be expressed as follows,

ε' values:

CNT+Pyrograf > CNT > CNT+VGCF > CNT+CB

ε'' values:

CNT > CNT+Pyrograf > CNT+VGCF > CNT+CB



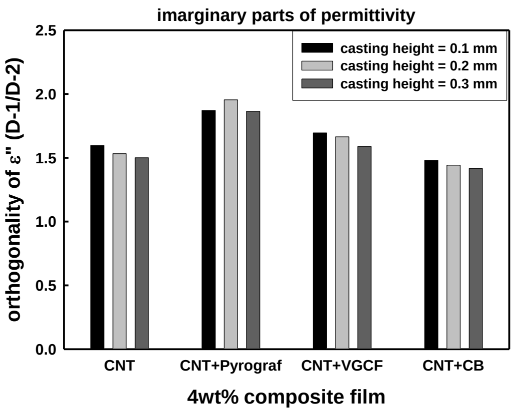


Fig. 6 Orthogonality of ε' and ε'' between D-1 and D-2 directions in films of various casting heights

Fig. 6 shows orthogonality of both ε' and ε'' at 10 GHz vs. casting height. In the observation of the orthogonality defined by the ratio of electric property in the two directions, the CNT+Pyrograf film presents the greatest orthotropic feature because of its hairy shape extended to about 100 m. In case of CB, adding spherical shaped CB in CNT was expected to decrease orthotropic feature, but the orthogonality of CNT+CB films is similar to that of CNT films.

The order of the orthogonality can be expressed below,

ε' values:

CNT+Pyrograf ~ CNT+VGCF > CNT ~ CNT+CB

ε'' values:

CNT+Pyrograf > CNT+VGCF > CNT ~ CNT+CB

The effect of the film thickness on the alignment was investigated by observing the orthogonality of electric property. Generally, the orthogonality is reversely proportional to the film thickness except for the CNT+Pyrograf film.

3.3 DC electric conductivity

Table 4 shows DC electric conductivity of the film. In all films, the conductivity of casting direction is higher than that of transverse direction, which is similar to those of AC electric property.

Table 4 DC electric conductivity of resin films

Sample No.	Thickness [mm]	Conductivity [S·m]	
		D-1	D-2
1 (CNT)	0.045	8.082	5.133
	0.098	11.530	7.341
	0.155	11.887	7.677
2 (CNT+Pyrograf)	0.049	1.894	1.041
	0.100	2.632	1.121
	0.172	2.400	1.299
3 (CNT+VGCF)	0.042	2.506	1.380
	0.094	3.594	2.223
	0.165	3.680	2.499
4 (CNT+CB)	0.044	3.089	1.924
	0.094	4.043	3.205
	0.152	4.264	3.069

It must be noted that the order of the DC electric conductivity is quite different from that of AC electric property as below,

CNT > CNT+CB > CNT+VGCF > CNT+Pyrograf

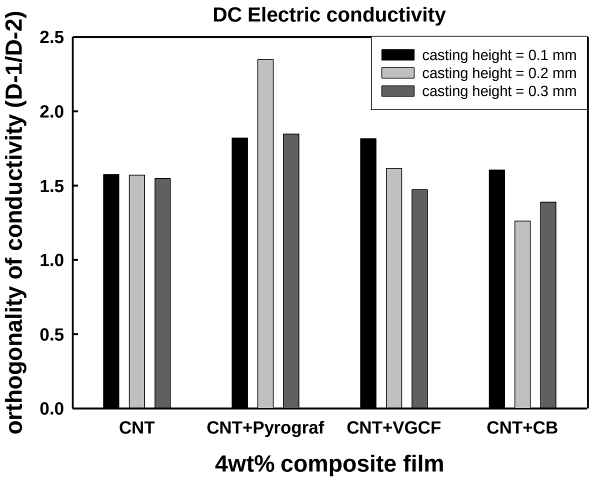


Fig. 7 Orthogonality of conductivity of various thickness films

Fig. 7 shows the orthogonality of conductivity. It seems that the DC electric conductivity has the same tendency with the complex permittivity shown in Fig. 6.

4 Conclusion

The nanocomposite resin films were prepared with epoxy resin and carbon nano materials of different aspect ratio and shape to observe orthotropic electrical property during tape casting process. The alignment of the carbon nano materials were observed through the SEM images of cross sections along casting and transverse directions. AC (8.2 ~ 12.4 GHz) and DC electric property of these nanocomposite films was measured.

The order of the electric property in AC electric field according to the carbon nano materials is CNT > CNT+Pyrograf > CNT+VGCF > CNT+CB. But, in DC electric field, the order was changed to be CNT > CNT+CB > CNT+VGCF > CNT+Pyrograf.

We compare the electric property in the casting direction with that in the transverse direction of films in AC as well as DC electric field. Every nanocomposite films have orthogonality of electric property greater than 1.4 (D-1/D-2). The films including two different kinds of CNF have a relatively high orthogonality. Generally, the orthogonality is reversely proportional to the film thickness except for the CNT+Pyrograf film.

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