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Reinforcement on Properties of Poly(vinyl alcohol) Films by Embedding Functionalized Carbon Micro Coils

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Carbon micro coils (CMCs) were hybridized with poly(vinyl alcohol) (PVA) through esterification reaction. The mixing of as-prepared CMC hybrid with polymer (PVA) matrix was effective to prepare PVA film where the functionalized CMC was homogeneously dispersed and embedded. The presence of CMCs in PVA film heightened the glass transition temperature of PVA. Results of tensile stress and electrical conductivity indicated that overall mechanical and electrical properties of PVA film were enforced by embedding CMC, depending on increase of the CMC concentration. These properties were further reinforced by prefunctionalization of CMC by PVA, because CMC can have an affinity to PVA in matrix through PVA immobilized on CMCs. However, mechanical and electrical properties for both nonfunctionalized and functionalized composites were depressed above a certain CMC concentration, indicating the self-orientation of CMC in the matrix, different from the behavior of carbon black.

Keywords: Carbon Micro Coil, Poly(vinyl alcohol), Hybrid, Composite, Film, Tensile Analysis, Electrical Conductivity, Scanning Electron Microscope, Thermal Gravimetric Analysis.

1. INTRODUCTION

Since 1980s, new carbon families like fullerene and carbon nanotubes (CNTs) have been discovered. These new materials are gathering great attentions since they have unique characteristics, and many applications have been proposed for mechanical and electrical usages. Especially, their composites with polymers were regarded as novel functional materials, and combinations with a variety of polymers were reported.^{1–4} In recent years, several studies have focused on composites of poly(vinyl alcohol) (PVA) loaded with CNTs or carbon fibers.^{5–17} A significant enhancement of the mechanical properties of the PVA has been obtained at low CNT loading.^{8, 12} On the other hand, PVA composites with CNTs and carbon filaments up to 5 wt% exhibited a nearly constant conductivity in the temperature range from 20–220 °C.¹³

Carbon micro coils (CMCs) are an amorphous carbon material and have super-elastic properties owing to a spiral structure with coil diameters in micrometer.^{18,19} CMCs can be extended by 3–15 times and contracted to the original coil length.²⁰ Therefore, CMCs are available to improve the mechanical, thermal and electrical properties of polymers.

ite with CMC, the reinforcement of Young modulus was attributable to the unique conformation of CMCs.²² The electrical resistivity of the rubber composites with CMC increased with the compressive or tensile strain, and the change in resistivity was found to be much higher than that of other composites involving carbon fibers and carbon blacks.²³ CMCs are thus valid as highly attractive additives due to these particular characteristics which are applicable as sensors and actuators. The aim of the present work is to characterize composite films of CMCs with PVA matrix. PVA, a useful water-soluble polymer, has been widely studied and utilized

It was reported that only a 1–2 wt% addition of CMC in poly(methylmethacrylate) beads resulted in strong electro-

magnetic wave absorptivity.²¹ On the epoxy resin compos-

as fibers or film matrices.^{5–17} The present films are prepared by embedding CMCs in PVA matrix, where CMCs were preliminarily hybridized with PVA. It is assumed that the functionalization of CMCs by PVA facilitates their dispersion in the polymer matrix, improving the homogeneity of the composite film. Moreover the morphological, mechanical, electrical and thermal properties of the composite films should be more progressed than the dispersion of nonfunctionalized CMCs in PVA matrix. The load-electrical behaviors should be assured by well

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dispersed CMCs in the matrix, and these characteristics are beneficial to fabricate tactile sensors. The composite of surface-hybridized CMC where the high electrical conductivity is expected should be useful in its application to fuel cells.

2. EXPERIMENTAL DETAILS

2.1. Materials

CMC was prepared according to previously reported procedure.^{18, 19} PVA ($MW \sim 13000 - 23000$, 98% hydrolyzed) was purchased from Aldrich. N,N'-dicyclohexylcarbodiimide (DCC, 99%) and 4-dimethylamino pyridine (DMAP, 99%) were obtained from Acros Organics, USA. 1-hydroxybenzotriazole (HOBT), HNO₃ (60%), and dimethyl sulfoxide (DMSO, 99.5%) were commercial products. All reagents were used as purchased. Ultra-pure (18.2 M Ω cm) water was used throughout whole experiments.

Oxidized CMC (acid-treated CMC) was prepared according to a previously reported procedure, where acid-treatment was carried out for 12 h.²⁴ The acid-treated

CMC was characterized by infrared absorption spectra, X-ray photoelectron spectroscopic spectra, and thermal analysis. Then CMC was hybridized with PVA through a carbodiimide-activated esterification reaction²⁵ as shown in Figure 1. In a typical reaction, DCC (400 mg), DMAP (66 mg), and HOBT (130 mg) were dissolved in DMSO (15 cm³), and an oxidized CMC (166 mg) was added to this mixed solution, followed by stirring for 1 h (solution A). Separately PVA (166 mg) was dissolved in DMSO (10 cm³) and stirred up to 1 h at 65 °C (solution B). Then the solution B was added into a solution A, and the mixture was stirred (850 rpm) for 48 h and filtered through a Advantech (Japan) membrane filter (PTFE polymer, pore size 0.2 μ m). The hybridized residue (hybrid CMC) on filter was rinsed by acetone and water and dried overnight in a vacuum oven at 50 °C.

2.2. Preparation of Composites

Composite films of hybrid CMC with PVA were prepared by a wet-casting method. In typical procedure, PVA (195 mg) and hybrid CMC (5 mg) (2.5 wt% = [hybrid CMC/(PVA + hybrid CMC)]) were mixed with



Fig. 1. Preparation processes of hybrid and composite samples. (Top) esterification of acid-treated CMC with PVA. (Bottom) composite preparation of PVA with CMC.

water (5 cm³). After the mixture was stirred for 6 h at 90 °C, it was dropped onto a Teflon sheet with an aluminum frame (3.5×6.5 cm). After the composite solution was uniformly spread within aluminum frame, it was kept inside a vacuum oven for 3 h at 60 °C. The obtained composite film was recorded average thickness of 0.07 mm by a Teclock (Japan) thickness gauge. By similar way, composite films with 0, 2.5, 5, 6.5, 8 and 10 wt% CMC content were prepared. After that, the films were cut off to the required size and shape. For tensile and conductivity measurements the specimens were shaped dumbbell-like (with width of 4 mm). Composite films of pristine CMC with PVA and a pristine PVA film were also prepared according to the procedure as above.

2.3. Measurements

Thermal gravimetric analysis (TGA) experiments were carried out using a TGAQ500 equipment (TA Instruments, USA), where powders (4.5 mg) (pristine and hybrid CMCs



Fig. 2. Top: TGA curves of CMC and PVA. (a) Pristine CMC, (b) hybrid CMC, (c) pristine PVA. Bottom: A SEM image of hybrid CMC.

and pristine PVA) were heated at a scan rate of 10 °C/min from 25 to 800 °C under N₂ streaming. The morphology of powders (hybrid CMCs) was analyzed using a scanning electron microscope (SEM, S-3000N Hitachi, Japan) at accelerating voltages of 20 kV. For composite films of CMC and PVA, following measurements were carried out besides SEM. Morphology was checked by an optical microscope (Nikon). Differential scanning calorimetric (DSC) experiments were carried out using a Perkin Elmer Diamond instrument. After PVA and composite films were stored in desiccators under CaCl₂ up to one week, they (4.5 mg) was used for DSC measurements at a scan rate of 10 °C/min on cooling at 230–25 °C after heating at



Fig. 3. Optical micrographs of PVA films. (Top) pristine PVA, (middle) pristine CMC composite, (bottom) hybrid CMC composite.

25–230 °C at the same rate under N_2 streaming at flow rate of 30 cm³/min. The temperature and heat flow were calibrated with indium and zinc standards. Dynamic mechanical analysis (DMA; 01db-Metravib-DMA50N, AREVA group, France) curves for rectangular films of 25 mm length and 5 mm width were recorded using shear mode by heating from -10 to 150 °C at 1 Hz. Tensile measurements were carried out by using a tensile testing machine (Lloyd Instruments, UK) instrument at room temperature. The dumbbell shape specimen (gauge length = 21 mm) was pulled at the rate of 2 mm/min; reported values represent an average of at least five times measurements for each sample. The electrical conductivity of the dumbbell shape specimen was measured by a DMM-85 conductmeter (DHA, Taiwan), where maximum conductivity values were chosen for each samples.

3. RESULTS AND DISCUSSION

To determine the thermal stability of hybrid CMC (CMC hybridized with PVA), TGA measurement was performed

under nitrogen atmosphere in comparison with pristine CMC and PVA (Fig. 2(top)). While the pristine CMC remained nearly constant weight even with heating up to 800 °C, the weight of hybrid CMC decreased gradually from ~100 °C and sharply from ~350 °C and became almost constant after ~460 °C. The first small weight drop (~4 wt%) is due to the adsorbed contamination like solvent or organic molecules but the second drop (~10 wt%) comes from the burn of esterified PVA on CMC. On the other hand, a TGA curve of pristine PVA exhibited three main steps of weight loss except the loss by contamination: Major decomposition was at ~270 °C (~44 wt% loss) and minors were at ~470 °C (~8 wt% loss) and ~575 °C (~6 wt% loss).

By comparing these values of weight loss with that of hybrid CMC, the first finding is that a weight loss from hybrid CMC originates in interfacial (ester) linkage of CMC with PVA, different from pristine PVA that is burned at different chemical units. The second one is that organic component in hybrid CMC is about 17%. This result can be compared with the content (12%) of carboxylic acid



Fig. 4. SEM micrographs of PVA films. (a) Pristine CMC composite, (b) hybrid CMC composite. CMC content: (top) 2.5%, (bottom) 10%.

on CMC.²⁴ The increase of the organic component after esterification is close to the increase (1.6 times) in molecular weight after reaction of polymer unit with carboxylic acid on CMC, indicating a large number of hydroxyl groups of polymers are esterified with carboxylic acid on CMC. SEM imaging was employed to visualize the hybridized CMCs and was shown in Figure 2(bottom). There were no distinguishable textures except CMCs and the surface of CMCs was rather smooth as well as pristine CMC. This means that hybridized PVAs have stuck to CMC. This result is consistent with that from TGA measurement described above.

CMCs hybridized with PVA were found to be dispersed in water and no aggregated domains of CMCs were



observed in the film of hybrid CMC composite (hybrid CMCs in PVA matrix) but such domains happened in pristine CMC composite (pristine CMCs in PVA matrix), as directly evidenced by optical microscopic images (Fig. 3),



Fig. 5. DSC (cooling) thermograms (top and middle) and a DMA curve (bottom) of PVA films. (a) pristine PVA, (b) pristine CMC composite, (c) hybrid CMC composite.

Fig. 6. Mechanical measurements of PVA films. (A) stress-strain curves (inset: a tensile specimen). (B) Young's modulus, (C) tensile strength, (D) strain at a breakage as a function of CMC content. (a) pristine PVA, (b) pristine CMC composite, (c) hybrid CMC composite.

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where the texture of pristine PVA (without CMCs) is included. It seems that the hybrid CMC composite exhibits better homogeneity compared to pristine CMC composite. These differences could be reflected their thermal, mechanical and electrical properties.

When the films of CMC composites (pristine and hybrid) were prepared at two CMC contents, it is obvious from SEM images in Figure 4 that CMCs were embedded in PVA matrix at low content (2.5%) of pristine composite. When the CMC content was increased (to be 10%), CMC texture could be seen on the surface of PVA film and the surface became rough. However, in hybrid composite, CMCs were almost embedded in PVA matrix both at lower and higher CMC contents. Actually, hybridized CMCs were better dispersed in the PVA matrix even at high CMC content owing to the affinity of PVA in hybrid with PVA matrix.

DSC measurements on cooling process were carried out to check out crystallization (Tc) and glass-transition (Tg) temperatures of polymer in the composite films. As seen in Figure 5(top), a main exothermic peak related to crystallization was observed at 191.4 °C for PVA films without and with CMC, indicating that there is no substantial changing in crystallization temperature of PVA after embedding of CMC. Although the location of Tg temperature of PVA films was not so clear from DSC results, it could be estimated from the cross section of two linear lines (Fig. 5(middle)). The Tg value (78.2 °C) for pristine PVA film was lower than values (93.0 and 99.4 °C, respectively) for pristine and hybrid CMC composites. This tendency agrees with a previous report for single wall carbon nanotube/PVA composites.⁸

The more accurate transition temperature of the PVA films can be further evaluated from DMA measurement. In this instance, the Tg value appears as a peak in tan δ at corresponding temperature (Fig. 5(bottom)). While the Tg temperature was at 77.2 °C for the pristine PVA film, those for the pristine and hybrid CMC composites were

Table I. Young's modulus, tensile strength and electrical conductivity of PVA and composite films.

Film	CMC content (%)	Young's modulus (MPa)	Tensile strength (MPa)	Electrical conductivity (S/mm)
PVA	0	78.9	5.3	0
Pristine CMC composite				
-	2.5	101.2	8.7	0
	5	129.1	9.0	143.4
	6.5	284.3	12.4	150.2
	8	256.7	9.2	55.6
	10	143.3	5.9	40.4
Hybrid CMC composite				
	2.5	143.2	10.5	0
	5	151.5	11.8	0
	6.5	358.0	16.4	90.6
	8	373.0	14.6	185.8
	10	316.7	13.8	165.5

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shifted to 91.4 and 97.6 °C respectively. These values and the tendency of the shift are consistent with those from DSC analysis.

In the Tg region, the CMCs act as a resistance to viscous flow of the polymer chains, and resultingly the Tg value of the both CMC composites becomes higher than that of the pristine PVA film. Hybrid CMCs are expected to have an affinity to PVA matrix through the hydrogen bonding with PVA in functionalized CMC. Therefore, the Tg value of hybrid CMC composite is higher than that of pristine CMC composite. Yoonessi et al.²⁶ have reported that the increasing crosslinking density of phenolic resin could be coincided with the increase in Tg value, as demonstrated from progressive shift of tan δ peaks to higher temperature with more content of carbon nanofiber.

The mechanical properties of hybridized CMC composite were measured on dumbbell-type films (see Fig. 6(A), inset) at room temperature and compared with those of pristine CMC composite and pristine PVA film (Fig. 6(A)). Young's modulus can be calculated as the initial slope





Fig. 7. Electrical conductivity test of PVA films. (Top) a photograph of electrical conductivity measurement. (Bottom) electrical conductivity at different CMC contents. (a) pristine PVA film, (b) pristine CMC composite, (c) hybrid CMC Composite.

of a stress versus strain curve, and the tensile strength equals to a broken stress on the same curve. Such data are listed in Table I and plotted in Figures 6(B and C) as a function of CMC content. Young's modulus and tensile strength increase in the order of pristine PVA film < pristine CMC composite < hybrid CMC composite. The reason for higher mechanical properties of composites is due to the affinity between reinforcing materials (CMCs) and polymer (PVA) matrix. Then it should be noticed that the affinity in hybrid CMC composite is stronger than that in pristine CMC composite from the reason explained above.

Figure 7(top) depicts the measurement of electrical conductivity between both edges of dumbbell-type films. The electrical conductivity of pristine CMC composite was null at 2.5% CMC content but it was heightened around 150 S/mm at 5 and 6.5% and diminished around 40 S/mm at 8 and 10%, as seen in Figure 7(bottom). On the other hand, hybrid CMC composite up to 5% took non-conductivity and the highest conductivity value was observed at 8% but it decreased after that. The increase in the conductivity with increasing in CMC concentration implies the occurrence of so-called "percolation phenomenon." Xu et al.²⁷ have reported percolation threshold for composites containing carbon blacks in a polyethylene matrix. Such a report describes that the percolation threshold of less dispersed carbon black composite occurs

at earlier stage than that of highly dispersed carbon black composite. This tendency is similar to the present result, where heterogeneously dispersed pristine CMC composite generates percolation at low CMC concentration than homogeneously dispersed hybrid CMC composite.

Cui et al.²⁸ have reported that the increase of carbon black content in polypropylene/Novolac blends makes carbon black more crowded, leading to slow decrease of volume resistivity. The volume resistivity decreases dramatically in the vicinity of the percolation threshold, where the transition from insulator to conductive material occurs. Although carbon nanofibres were used as reinforcing fillers in polymer (epoxy resin) matrices,²⁹ as well as carbon black, CMCs could also reinforce the polymers (epoxy resin and silicon rubber) and the degree of reinforcement was much larger than that by carbon black and carbon nanofibres.^{22, 23} It is noted from the present work that not only the reinforcing effects of CMCs embedded in PVA can be expected as prevalent fillers but also the effect is further reinforced by immobilization of PVA to CMC. The latter effect has never been reported previously.

It should be noticed that the increasing content of CMCs was effective to improve the mechanical and electrical properties of PVA matrix at CMC contents up to 6.5–8% but the further increase in content of CMCs raised the depression of such properties, as described above



Fig. 8. Optical (top) and SEM (bottom) micrographs of tensile-fractured PVA films. (a) Pristine CMC composite, (b) hybrid CMC composite. Arrows indicate the direction of tensile-fracture.

(Figs. 6(B, C) and 7(bottom)). This means that the promotion of both mechanical and electrical properties in CMC composites is diminished above certain CMC content, although this behavior has never been observed before. Then the aspect of CMCs in composites is assumed as below.

At low CMC contents below percolation threshold, CMC fillers are isolated. Then the tensile property of the composites slightly increases but their conductivity is not generated yet. From the percolation threshold at 2.5-5% CMC contents, since the CMC fillers begin to form networks in the films, the tensile property increases and the conductivity starts rising. At the higher CMC content, CMC fillers can become to be agglomerated with self-orientation each other because of the abundant existence of CMCs with anisotropic structure and steric hindrance between them. This aspect of CMCs will reduce mechanical and electrical properties of composites. The filler agglomerates in the film may also cause breakdown of stress at high strains as seen in Figure 6(A). The threshold strain of breakage decreased with CMC content (Fig. 6(D)). This tendency was more obvious for pristine CMC composite than hybrid one because of stronger Van der Waals attraction between pristine CMCs (without immobilized PVA) in the PVA film.

To further characterize the morphological aspect in the composites, SEM observations were performed on fracture edges of composites ripped at around 50% strain (see Fig. 8(bottom)). In both cases of pristine and hybrid CMC composites, the PVA fibrils were partly oriented along the stretching direction. Figure 8(top) shows optical microscopic images of the same specimens as SEM measurement. CMCs in hybrid CMC composites visualized as black textures were better aligned to the stretching direction than in pristine CMC composites.

4. CONCLUSION

Physical properties of polymer matrix depend on size, shape, concentration, distribution, and surface character of fillers. The dispersion state and the concentration of fillers especially play an important role in mechanical and electrical properties of polymer composite. The present study has explored hybridization of CMC with PVA via esterification reaction and embedding of as-prepared hybrid in PVA matrix. DSC and DMA results displayed heightening in the glass transition temperature of PVA after incorporation of CMCs in PVA. Tensile analysis confirmed that CMC composites resulted in the increase in Young's modulus and tensile strength from pristine PVA film by incorporating CMC, depending on CMC concentration. On the other hand, electrical conductivity of composites increased with CMC concentration after the percolation threshold.

Similar behavior has been reported on some combinations of fillers (carbon black, carbon fibres, and carbon nanotubes) in different polymer matrices, where fillers are simply blended in polymers.^{4, 22, 23, 27–29} However, in the present work, CMC was pretreated by chemically binding with PVA and it was discovered that hybrid CMCs with PVA promoted the further reinforcement on properties of PVA matrix as compared to a case of simple blend system, due to the affinity between PVA immobilized on CMCs and PVA in the matrix.

The direct affinity through hydrogen bonding between PVAs in hybridized CMCs and in polymer matrix should cause more compatible dispersion of CMCs in the hybrid CMC composite than in the pristine CMC composite, allowing more uniform (homogeneous) distribution of CMCs without segregation. This structural (morphological) aspect substantially effects further enhancement on the CMC-reinforced mechanical and electrical properties of composites which should be provided by the extent of stress-strain curve and electrical conductivity of the PVA matrix. This suggests that it is crucial to prepare homogenous composites, although this has never reported in the previous investigation. The present results demonstrate that CMCs functionalized by hybridization can be considered as novel fillers in the matrix for reinforcement of polymer properties.

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Received: 20 January 2010. Accepted: 18 February 2010.

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