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Electrical and mechanical characterization of stretchable multi-walled carbon nanotubes/polydimethylsiloxane elastomeric composite conductors

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ABSTRACT

Stretchable, elastomeric composite conductor made of multi-walled carbon nanotubes (MWNTs) and polydimethylsiloxane (PDMS) has been fabricated by simple mixing. Electrical percolation threshold, amount of filler at which a sharp decrease of resistance occurs, has been determined to be ~0.6 wt.% of MWNTs. The percolation threshold composition has also been confirmed from swelling experiments of the composite; the equilibrium swelling ratio slightly increases up to ~0.6 wt.%, then decreases at higher amount of filler MWNTs. Upon cyclic stretching/release of the composite, a fully reversible electrical behavior has been observed for composites having filler content below the percolation threshold value. On the other hand, hysteretic behavior was observed for higher filler amount than the threshold value, due to rearrangement of percolative paths upon the first cycle of stretching/release. Finally, mechanical moduli of the composites have been measured and compared by buckling and microtensile test. The buckling-based measurement has led to systematically higher (~20%) value of moduli than those from microtensile measurement, due to the internal microstructure of the composite. The elastic conductor may help the implementation of various stretchable electronic devices.

1. Introduction

Electronics having unusual form factor, called stretchable electronics, is rapidly developing field in recent years [1]. Contrary to conventional electronic devices/circuits fabricated by planar processing technologies, stretchable electronic components can be conformed onto complex, curvilinear surfaces while maintaining preset performance without failure upon such mechanical deformation. In view of electronic devices, three different categories of materials, drastically different in their electrical behavior, are essential; conductors, semiconductors and insulators. Especially, the stretchable conductors are required for electrical contact in each device, interconnection among devices, as well as connection between devices/circuits and outside world. Until now, 'shape engineering' of stiff metal film on elastomer by buckling has been the mainstay of elastic conductors, such as serpentine metal film embedded in elastomer [2] or buckled, wavy thin metal on elastomer surface [3]. These approaches depend on the change of three-dimensional shape of stiff metal film upon the application of external strain. In other words, the elastic conductor materials themselves are *not* stretchable at all, while their predesigned shape changes upon external mechanical stimuli, for example, from sinusoidal wavy to flat configuration in the case of buckled metal film approach. Recently, a few approaches [4–8] have been published to make inherently stretchable conductor, mostly blending conductive nanomaterials (metal nanoparticles, carbon fiber, carbon nanotubes, etc.) with elastomer. The elastomeric composite conductors indeed showed improved electrical performance, maintaining elastic properties up to acceptable level.

Since their discovery in 1991 [9], carbon nanotubes (CNTs) have been the choice of materials in various applications, ranging from nanoelectronics, sensors to even nanoprobes for high-resolution imaging [10] due to their excellent chemical and physical properties such as strength, modulus, and electrical and thermal conductivities. Until now, one of the most promising and practical applications of CNTs is their use as reinforcing filler in polymer matrices, with the outstanding improvement in mechanical, thermal and electrical properties [11]. Especially, the high aspect ratio (i.e., length to diameter ratio) of carbon nanotubes can reduce the electrical percolation threshold significantly, compared to nanoparticles or nanorods/nanowires [4–8].

Silicone-based materials, especially polydimethylsiloxane (PDMS), have been widely used not only in traditional applications such as sealants and protective insulating coatings [12] but also in emerging applications such as a stamp material for soft lithography, microfluidics, and microelectromechanical systems [13]. The electrically conducting CNT/PDMS composite has been shown to

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be applied in stretchable electronics [7], compliant electrodes for dielectric actuators (DEAs) [14–16], multifunctional sensors [17], heat-dissipating materials [18], as well as reinforcing fillers in high strength, light weight composite materials [19–23].

Recently, mechanical buckling-based method for the measurement of Young's modulus of a material has been proposed and found to be a simple, fast, and low-cost method [24]. The method is based on the well-known mechanical phenomenon, called buckling, which means catastrophic failure of constructions and thus has long been studied in structural mechanics field. The seminary work [25], however, has led to advantageous utilizations of the mechanical buckling, such as stretchable electronics [26] and buckling-based metrology. The buckling-based metrology has been applied to various materials: amorphous or semi-crystalline polymer thin films [24,27], ultrathin polymer films [28], polymer brush [29], polyelectrolyte multilayer [30], nano or molecular-scale materials [31–34], and organic electronic materials [35]. Further, the method has been shown to be applied for the mechanical characterization of compliant substrate materials such as elastomer or hydrogels [36], using 'sensor' film having known mechanical properties.

In this work, MWNT/PDMS composite elastomer has been fabricated by simple mixing, or without any chemical treatment of the filler MWNTs. The electrical resistance as a function of filler content has been used to find the percolation threshold value of MWNTs in the composite. The percolation threshold value, determined to be ~0.6 wt.% in this work, has been found to have profound effect on the solvent swelling behavior, as well as the electrical behavior upon cyclic stretching/release. Hysteresis in electrical resistance of the composite has occurred in composites having higher filler content than the percolation threshold, while composites having filler content less than the threshold value showed reversible electrical resistance upon repeated stretching/release. Also, the equilibrium swelling ratio has been larger than unfilled, pure elastomer for composites having filler amount less than the threshold, but the swelling ratio has decreased as the filler content increases above the threshold. Finally, the mechanical moduli have been characterized by both uniaxial microtensile test and buckling method. The mechanical properties of the composite has improved with increasing MWNT content, in spite of no surface treatment of the MWNT and thus rather poor dispersion in the elastomer matrix. Further, the modulus value determined from both approaches showed systematic disagreement; the buckling method leads to 20–30% higher value than the microtensile test. The discrepancy will be discussed in terms of testing method and materials' microstructure.

2. Materials and methods

2.1. Materials

The multi-walled carbon nanotubes (purity 90%, diameter 15–20 nm, length 30–50 μm) were kindly supplied from EM-POWER Co. Ltd. (Korea), and used as-received. The polystyrene (M_w = 35,000 g/mol, PI = 2–3, Sigma) was dissolved in toluene and spun on Si wafer substrate. The Si substrate was wet-cleaned in acetone, isopropyl alcohol, and de-ionized water in ultrasonic bath for 5 min., respectively. The thickness of PS film on Si was 195 nm (±5 nm).

2.2. Fabrication of MWNT/PDMS composite

MWNT/PDMS composite was fabricated by manually mixing MWNT into PDMS (Sylgard 184, Dow) and stirring the mixture for more than 10 min. Although there have been many reports on the enhanced dispersion of nanotubes in polymer matrix by chemical functionalization of the nanotube surface, some literatures [37, for example] suggest that the interaction between methyl group in matrix and π-bond on the nanotube surface be enough to disperse nanotubes in the matrix. The amount of MWNT filler in the composite was varied from 0.2 to 1.4 wt.%. When the filler content exceed 1.4 wt.%, the mixture became too viscous to process it further. After mixing, the composite was cast on flat surface (ex: Si, glass, petri dish) with desired thickness and then evacuated in vacuum desiccator to remove entrapped air bubbles. As will be discussed later, as the MWNT content increases, larger than ~0.8 wt.% in our case, the cured composite elastomer samples still have some air bubbles, which affect the value of mechanical modulus depending on test method. Finally, the cast composite was cured at 70 °C for 2 h in oven.

2.3. Characterization

The dispersion state of MWNT fillers in PDMS matrix was examined by scanning electron microscopy (SEM) (HITACHI, TM-1000) and atomic force microscopy (AFM, Asylum MFP 3D). Equilibrium swelling experiments were done at room temperature on samples with dimension of 50 mm * 50 mm * 50 mm (length, width, and thickness, respectively). The samples were put into a good solvent, toluene, and the dimension of swelled samples was measured by vernier caliper after 24 h. The swelling ratio was calculated from the volume of the sample in the unswollen and swollen states. Electrical resistance was measured using high-resistance meter (ADVANTEST, R8340A). For composite samples having relatively low resistance, two-terminal current–voltage were measured by semiconductor parameter analyzer (HP, 4156A) and compared to the results from high-resistance meter. The two methods yielded similar results within experimental error.

A microtensile tester (Linkam, TST 350) was used to measure the stress–strain behavior of the MWNT/PDMS composites. The tensile tests were carried out at constant speed of 1.0 mm/s at room temperature. For the Young's modulus from the microtensile test, the linear portion of stress–strain curve, typically up to ~50% strain, was used.

In buckling-based method, we used 195 nm-thick PS film as a sensor. The hydrophillicized Si substrate (by uv/ozone treatment for 20 min.) with spun-cast PS film on it was put into DI water to float the PS film. Then the released PS film on water was picked-up on composite elastomer surface. The PS/composite sample was loaded onto home-made compression stage and compressed gradually to generate buckled surface. The compression buckling process was done under optical microscopy (OM, Olympus BX51). Note that excessive compressive strain on the PS/composite sample can lead to delamination of PS film off the composite substrate, unless special steps are taken to make good enough adhesion between the PS film and the composite substrate. The compressive strain was thus maintained at lowest level, typically ~2%, to prevent film delamination and make observable buckled surface at the same time. The buckling wavelength (λ) was measured from the OM images by measuring distance along many waves (typically more than 10 waves) divided by the number of waves contained, and at more than five locations on sample surface, which yields quite accurate value of buckling wavelength due to averaging effect (the wavelength value from OM was compared to those from AFM, and showed no noticeable difference). The wavelength (λ) values were used to calculate the Young's modulus of composite substrate using the following equation:

$$\lambda = 2\pi h \left(\frac{\bar{E}_f}{3\bar{E}_s} \right)^{1/3} \quad (1)$$