Journal of the Korean Ceramic Society
Vol. 44, No. 4, pp. 198~201, 2007.

Carbon Nanotube/Nafion Composites for Biomimetic Artificial Muscle Actuators

Se-Jong Lee,† Hyun Woo Yoon, and Deuk Yong Lee*

Department of Advanced Materials Engineering, Kyungsung University, Busan 608-736, Korea
**Department of Materials Engineering, Daelim College of Technology, Anyang 431-715, Korea*

(Received March 12, 2007; Accepted March 13, 2007)

ABSTRACT

Multi-walled carbon nanotube (M-CNT)/Nafion nanocomposites were prepared by solution casting to elucidate the effect of M-CNT addition, from 0 to 7 wt%, on the viscoelastic behavior of the composites. The M-CNT bundles induced by the Nafion polymer were determined to be uniformly distributed for the 1 wt% M-CNT/Nafion nanocomposites. The 1 wt% M-CNT/Nafion composite exhibited the highest blocking stress of 2.3 kPa due to its high elastic modulus of 0.485 GPa. From a dynamic mechanical analysis, the 1 wt% M-CNT had the highest storage and loss moduli compared with the other samples in all frequency and temperature ranges. From the storage modulus data, the M-CNT loaded composites had similar T_g values near 120°C. The glass transition temperatures of the M-CNT loaded composites were 120°C (1 wt%), 117°C (3 wt%), 117°C (5 wt%), and 135°C (7 wt%), suggesting that the effect of the M-CNTs on the Nafion film begins at 1 wt%. Thus, it has been concluded that the 1 wt% M-CNT dispersed composite is attractive for actuator applications.

***Key words*: Carbon nanotube, Nafion, Nanocomposite, Dynamic mechanical analysis, Actuator**

1. Introduction

The increased demand for highly active, flexible, miniaturized sensors and actuators that produce a high power density and large force generation capabilities for biomedical applications and micro-robotics has fueled the development and introduction of carbon nanotube (CNT)/polymer nanocomposites.[1,2] The CNT/ionic polymer-metal composite (IPMC) nanocomposites have been produced widely using Nafion as a flexible polyelectrolyte matrix and a network of mobile positive and negative ions to optimize the CNT actuators.[3] IPMCs consist of a perfluorinated polymer electrolyte (Nafion) sandwiched by electroless-plated platinum (Pt) on both sides. The soft actuation of IPMCs was restricted by the mechanical and electrochemical fatigue associated with the underlying faradic intercalation-deintercalation process, resulting in a limited lifetime.[3-7] Single-wall carbon nanotube (S-CNT) sheets have been studied for implementation in electromechanical actuators, such as robotics, artificial muscles, and microscopic pumps, due to their excellent mechanical properties, electrical conductivity, and charge transfer properties.[1,2] The effectiveness of S-CNTs can be extended to the efficient and direct conversion of electrical energy into mechanical energy through a combination of quantum chemical and double-layer electrostatic effects. However, S-CNT sheets lead to a decrease in the net surface area available for double layer charging, electrochemical creep, and a low elastic modulus because they consist of nanotube bundles of 100-1000 nm joined by mechanical entanglements and van der Waals forces.[2]

To alleviate the aforementioned drawbacks, the S-CNT powder dispersed Nafion solution was cast to fabricate S-CNT/Nafion composite actuators. The successful dispersion of the purified S-CNT into Nafion demonstrated efficient actuation behavior.[3] Although an inferior stress generation capability and a reduction in the elastic modulus of the composites in comparison with pure S-CNTs were found, the actuation threshold of the S-CNT/IPMC nanocomposites at low doping levels (less than 5 wt%) of the S-CNTs was reported.[3] Multi-walled carbon nanotubes (M-CNTs)/Nafion nanocomposites were also studied because the synthesis of M-CNT is highly advanced, its quality and quantity are improved,[8] and various needs are satisfied, such as robotics, optical fiber switches, optical displays, prosthetic devices, sonar projectors, and microscopic pumps.[1]

The engineering tension/compression test is widely used to characterize a range of mechanical properties of agglomerates by constructing a stress-strain curve. However, these techniques cause irreversible damage to the structure of the agglomerates and their compacts. Consequently, information regarding the viscoelastic properties of the specimen can be limited.[9] Although the sample stiffness will depend on its modulus of elasticity, the modulus measured will depend upon the geometry choice and strain mode. Also, for materials that exhibit time-dependent deformation, the quoted modulus must include a time to be valid.

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†Corresponding author : Se-Jong Lee
E-mail : lsjong@ks.ac.kr
Tel : +82-51-620-4762 Fax : +82-51-622-8452

A powerful tool available to study the viscoelastic properties of materials is the dynamic mechanical analysis (DMA) because the DMA can simultaneously measure the time-dependent storage and energy loss. In addition, the DMA is a non-destructive technique that characterizes the viscoelastic properties of materials by applying a sinusoidal oscillating force (σ) to a sample and analyzing the response to that force, such as resulting strain (γ), stress, and phase lag (δ). The complex modulus (E^*) is expressed in Eq. (1):[9,10]

$$E^* = \frac{\sigma}{\gamma}cos(\delta) + i\frac{\sigma}{\gamma}sin(\delta) \qquad (1)$$

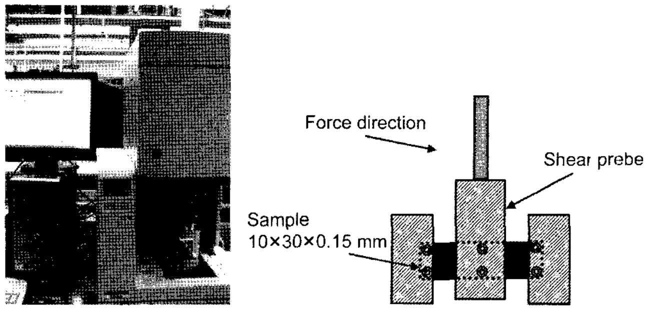
$$\tan\delta = E''/E' \qquad (2)$$

where $(\sigma/\gamma)cos(\delta)$ and $(\sigma/\gamma)sin(\delta)$ are the storage (elastic) (E') and loss (imaginary) modulus (E''), respectively. The storage modulus is an in-phase or elastic response, which is recoverable stored energy. The loss modulus is an out-of-phase or imaginary energy, which is irrecoverable, scattered energy. These different moduli allow better characterization of the material because we can examine the ability of the material to return or store energy (E') and lose energy (E''). The ratio of these effects (Eq. (2)) is referred to as damping (tan δ). Materials also show flow behavior even though the materials are known to be solid and rigid.

Multi-walled carbon nanotube (M-CNT)/Nafion nanocomposites were prepared by solution casting. Our previous studies[8,11,12] revealed that the M-CNT bundles induced by the Nafion polymer were uniformly distributed for the 1 wt% M-CNT/Nafion nanocomposites, exhibited a high elastic modulus, and improved the electromechanical properties. However, further M-CNT loading caused a heterogeneous distribution of M-CNT bundles and a negative impact on connectivity within the Nafion matrix, giving rise to poor actuation properties. It has been reported that the actuation properties of the nanocomposites were primarily governed by the M-CNT distribution behavior within the polymer matrix.[11] The modulus and glass transition (T_g) behavior of Nafion films and IPMCs loaded with various amounts of M-CNT were measured as functions of frequency and time using the DMA. Also, the variation of the stiffness and T_g in the shear mode was investigated to elucidate the viscoelastic properties of the composites.

2. Experimental Procedure

Multi-walled carbon nanotube (M-CNT)/Nafion nanocomposites were prepared by solution casting. The content of M-CNT is in the range of 0 to 7 wt%. The experimental procedure is described in detail elsewhere.[8,11,12] The specimen size was $10 \times 30 \times 0.15$ mm^3. After loading the specimen into the chamber, the DMA was performed using a Pyris Diamond DMA (Perkin Elmer, UK) with a Seiko Instruments Inc. analysis program in the shear mode. The DMA tester and a schematic diagram of the operational setup in the shear mode are shown in Fig. 1. The DMA frequency ranges from 0.01 to 100 Hz at temperatures varying from room temperature to 200°C with a heating rate of 3°C/min.



(a) (b)

Fig. 1. (a) A photograph of the DMA tester and (b) a schematic diagram of the DMA testing setup in the shear mode.

3. Results and Discussion

It has been reported that the 1 wt% M-CNT/Nafion composite exhibits the highest blocking stress of 2.3 kPa due to its high elastic modulus of 0.485 GPa,[11] as shown in Fig. 2. The storage and loss moduli of pristine Nafion, annealed Nafion, and M-CNT/Nafion composites are presented as a function of frequency in Fig. 3. The pristine Nafion film was obtained by only casting and drying, without further heat treatment. The annealed Nafion films were prepared by drying and subsequent annealing for 2 h at 70°C. It suggested that the 1 wt% of M-CNT had the highest storage modulus (E') compared with the other samples in all frequency ranges, which also indicated that it had the highest stiffness. From the experimental results, it can be deduced that 1 wt% of M-CNT may produce a strong blocking force, as demonstrated in Fig. 2. The loss modulus (E'') of the

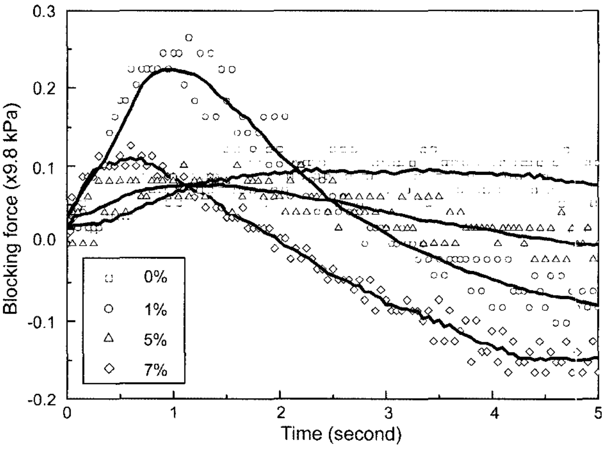


Fig. 2. Time response of the blocking force of the M-CNT/Nafion nanocomposite bending actuators.

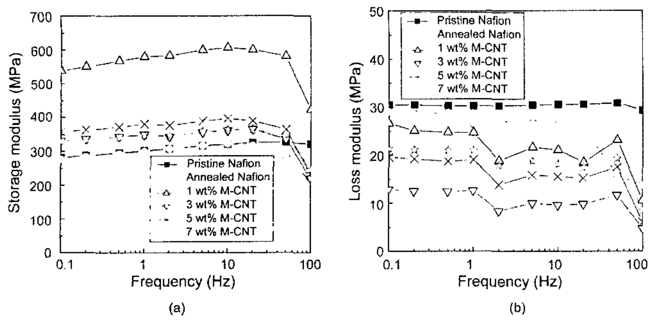


Fig. 3. The DMA results as a function of M-CNT content. The results are (a) the storage modulus and (b) the loss modulus with a frequency range from 0.01 Hz to 100 Hz.

1 wt% M-CNT/Nafion composite (Fig. 3(b)) was higher than that of the 3, 5, and 7 wt% of M-CNT composites. Therefore, it is evident that when the 1 wt% M-CNT loaded composite is an actuator, it has superior abilities to store and lose energy easily compared with the other composites. However, the loss modulus of the 1 wt% M-CNT dispersed composite was less than that of the pristine Nafion and the annealed Nafion.

The liquid Nafion solution refers to the solutions of Nafion Perfluoro-Sulfonated Ionomers (NPSI). Commercially available NPSI membranes are semicrystalline; therefore, they are not melt-processable since such supermolecular structures are resistive to flow. However, cast Nafion film exhibits morphological differences relative to as-received Nafion®; but, there is little information on cast Nafion membranes at the present time.

The temperature-scanned DMA results are given in Fig. 4. As anticipated, the highest storage and loss moduli at temperatures ranging from room temperature to 180°C were observed for the 1 wt% M-CNT loaded composites. The test was performed at 1 Hz. From the storage modulus data, the first transition peak shows T_g, which represents a major transition of materials. M-CNT loaded composites usually have similar T_g values near 120°C. The glass transition temperatures of the M-CNT loaded composites were 120°C (1 wt%), 117°C (3 wt%), 117°C (5 wt%), and 135°C (7 wt%) with an increasing amount of M-CNTs, suggesting that the effect of the M-CNTs on the Nafion film begins at 1 wt%.

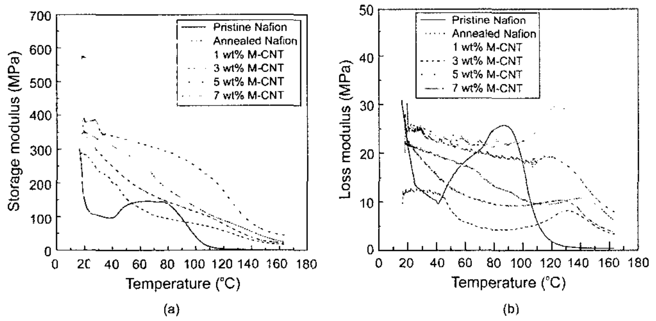


Fig. 4. The DMA results as a function of M-CNTs. The results are (a) the storage modulus and (b) the loss modulus using a temperature scan in the shear mode.

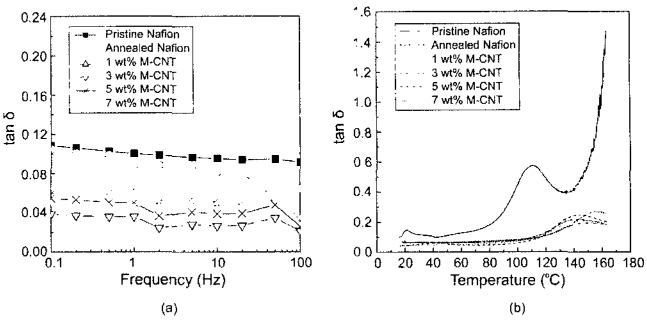


Fig. 5. Damping properties (tan δ) of the composites (a) with a frequency range from 0.01 to 100 Hz and (b) with a temperature scan in the shear mode.

Even if the contents of the M-CNT are above 1 wt%, there is no significant change in T_g. Thus, the 1 wt% M-CNT dispersed composite is attractive for actuator applications. The pristine Nafion film has two transition peaks: the initial peak at 79°C is the evaporation of residual solvents and the second at 109°C is the true T_g.

Damping is determined by the ratio of storage to loss modulus. The damping and dynamic elastic properties of various solid materials increase with frequency over a finite bandwidth, and the increase is weak if the damping is low.[13] The highest storage modulus represents the highest Young's modulus (stiffness), so the damping properties of the composites decrease, because stiffness is inversely proportional to damping. As anticipated, a lower tan δ(damping) was observed with frequency and temperature scans for the 1 wt% M-CNT dispersed composites, as shown in Fig. 5. Therefore, the addition of M-CNT into the Nafion matrix may enhance the stiffness, but the damping properties will decrease due to the increment of stiffness (storage modulus), which indicates that the damping is very low.

4. Conclusions

Multi-walled carbon nanotube (M-CNT)/Nafion nanocomposites were prepared by solution casting to elucidate the effect of M-CNT addition, from 0 to 7 wt%, on the viscoelastic behavior of the composites. The 1 wt% M-CNT/Nafion composite exhibited the highest blocking stress of 2.3 kPa due to its high elastic modulus of 0.485 GPa. From the dynamic mechanical analysis, the 1 wt% of M-CNT had the highest storage and loss moduli compared with the other samples in all frequency and temperature ranges. However, the damping of the composites was lowered due to the increase of the storage modulus (stiffness). From the storage modulus data, it was found that the M-CNT loaded composites had similar T_g values near 120°C. The glass transition temperatures of the M-CNT loaded composites were 120°C (1 wt%), 117°C (3 wt%), 117°C (5 wt%), and 135°C (7 wt%), which suggests that the effect of M-CNTs on the Nafion film begins at 1 wt%. Thus, it is concluded that the 1 wt% M-CNT dispersed composite is attractive for application in actuators.

Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-041-D00363).

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