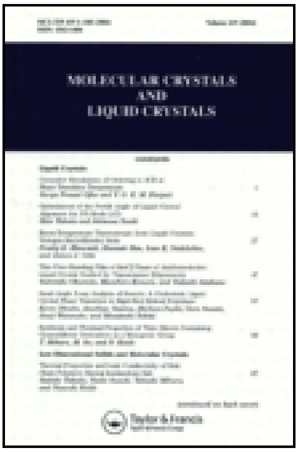

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Electromechanical Properties of P(VDF-TrFE)/CNT and P(VDF-TrFE)/Gr Composites

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Electromechanical Properties of P(VDF-TrFE)/CNT and P(VDF-TrFE)/Gr Composites

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*Electromechanical properties of poly (vinylidenefluoride-*co*-trifluoroethylene) (P(VDF-TrFE))/carbon nanotube (CNT), P(VDF-TrFE)/graphene (Gr) composites were investigated. The P(VDF-TrFE) composites with conductive fillers had the enhanced electromechanical strain response, which was affected by filler concentration but also by filler type. The strain was increased with the filler concentration. P(VDF-TrFE))/Gr composites had the higher strain response than the P(VDF-TrFE)/CNT composites at the same filler concentration level.*

Keywords Electromechanical strain; P(VDF-TrFE); carbon nanotube (CNT); graphene (Gr); composite

1. Introduction

Electroactive dielectric elastomers have taken a great deal of attention as potential actuators, owing to their outstanding properties such as high electromechanical actuation strain, fast response, high power-to-mass ratio and low cost [1–5]. However, the outstanding actuation performance has still been achieved at very high applied electric field strength. The high operational voltage is the biggest obstacle for real application.

Many dielectric elastomer composite systems with conductive fillers have been proposed in order to reduce the applied voltage by means of increasing the dielectric constant [6–8,12]. Zhang and coworkers reported that poly (vinylidenefluoride-*co*-trifluoroethylene-*co*-chlorofluoroethylene) composites with conductive carbon nanotubes achieved a massive actuation strain [6]. Such actuation performance enhancement was attributed to a higher dielectric constant of the composites in comparison to a matrix polymer. Huang and Zhang reported that poly (vinylidenefluoride-*co*-trifluoroethylene-*co*-chlorofluoroethylene) copolymer with polyaniline conducting polymer fillers showed a dramatic increase in the dielectric constant near the percolation threshold concentration and a big increase in the electromechanical actuation strain [7]. In contrast, Guiffard et al. claimed that though polyurethane with a small amount of conductive carbon powder fillers had almost the same

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dielectric constant as neat polyurethane, the electric actuation properties of the composites were significantly enhanced in the presence of the conductive fillers owing to the space-charge effect [8–14]. Nonetheless, the origins of the enhanced actuation of the composite systems with the conductive fillers are not yet fully understood.

This presentation introduces two types of carbon-based nanosized fillers of conductive carbon nanotubes (CNTs) with 1D morphology, and conductive graphene (Gr) with 2D morphology to poly (vinylidenefluoride-*co*-trifluoroethylene) (P(VDF-TrFE)) in order to investigate the effect of carbon-based nanofillers on the electric actuation in the nanocomposites.

2. Experimental

2.1. Materials and Sample Preparation

A poly (vinylidene fluoride –*co* – trifluoroethylene) (65/35wt%) (P(VDF-TrFE)) was purchased from Solvay Solexis Corp. The single wall carbon nanotubes (CNTs) with a trade name of P3-SWCNT were purchased from Sigma-Aldrich (purity > 90%). The graphenes (Grs) were chemically synthesized from graphene oxides. The grapheme oxides were prepared from purified natural graphite (45 μm, Sigma–Aldrich) by the Hummers method [15,16]. The graphene oxides were reduced to the graphene (Gr) using hydrazine hydrate ($N_2H_4 \cdot H_2O$ 98%). The PVDF/CNT and PVDF/Gr composites were prepared via solution blending in a DMF solvent. The well dispersed solution was rapidly precipitated in water in order to avoid the aggregation of the fillers, and the precipitates were dried in a vacuum oven. The 100 μm-thick composite films were made using a hot-pressing molding at 170âC. Circular gold electrodes with 60nm thickness were sputtered on both sides of the nanocomposites film.

2.2. Characterizations

The dielectric constant and dielectric loss of the composite film were measured by an impedence analyzer (HP1492A) at various frequencies ranging from 100 Hz to 100 kHz at room temperature. The electromechanical thickness strain of the composites was measured using two laser displacement sensors (Keyence LK-G80) under the application of a voltage step. The detailed thickness strain measurement setup was described in the previous literature [21]. For the electromechanical strain measurement, the composite films with gold electrodes were mounted between the rigid frames with a 20 mm diameter. The electric voltage was delivered to the film using a function generator, the Agilent 33250A, amplified by a factor of 1000 through a high-voltage lock-in amplifier, a AMT- 10B-10-LC, Precision Inc.

3. Results and Discussion

Figure 1a shows the TEM image of carbon nanotubes (CNTs) deposited from a 1 mg/ml DMF dispersion onto a carbon grid. CNT had the thin and long rod shape with high aspect ratio. The average diameter and average length of the CNTs were 4 nm and 1 μm. Figure 1b shows the AFM image of graphene (Gr) sheets deposited from a 1mg/ml DMF dispersion onto a silicone substrate. The Grs showed the 2D platelet morphology with 1 μm length. Gr had a 1nm step height from the surface of the substrate to the sheet.

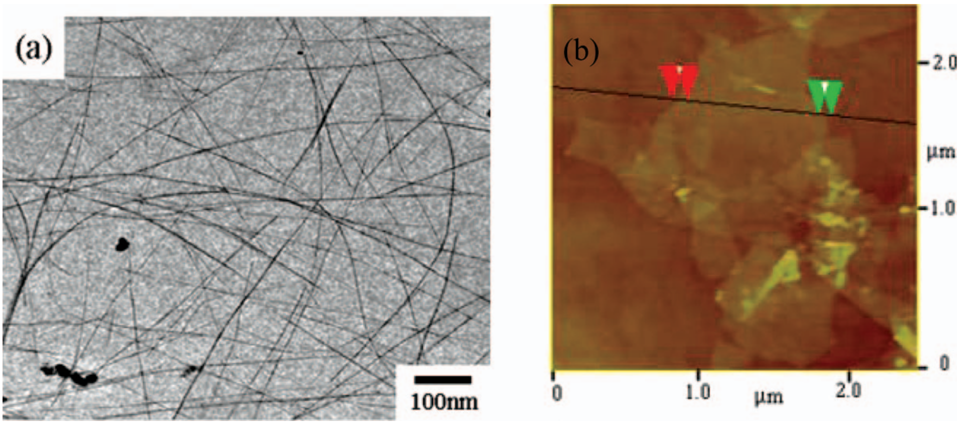


Figure 1. (a) Transmission electron microscopy image of the carbon nanotubes, and (b) AFM image of the graphene fillers.

Table 1 lists dielectric constants and dielectric losses of the P(VDF-TrFE)/CNT and P(VDF-TrFE)/Gr composite films with various filler content at various frequencies. The neat P(VDF-TrFE) film had a dielectric constant and dielectric loss of 9.7 and 0.017 at room temperature, respectively. The dielectric constants of the composite films increased with the filler concentration. The increase rate of the dielectric constant with filler concentration was different in each composite. The P(VDF-TrFE)/Gr composites showed faster increase rate of dielectric constant with the filler content than P(VDF-TrFE)/CNT composites. The P(VDF-TrFE)/CNTs with 0.1 wt% CNT fillers had a dielectric constant of about 11.4. In contrast, Dielectric constant of P(VDF-TrFE)/Gr with 0.1 wt% filler content were 13.0. Although the dielectric constant of the composites decreased with the frequency, this trend was observed in the whole frequency range. Interestingly, the dielectric loss factor of every composite in this work was kept low. The dielectric loss, resulting from the inelastic rotation of the dipoles in the sample under an applying electric field, relates to the internal energy dissipation as well as energy consumption during the electromechanical actuation [22]. The small dielectric loss of the P(VDF-TrFE) composites over the wide frequency range is also fascinating for energy efficient applications.

Table 1. Dielectric constants (K) and dielectric loss (D) of the P(VDF-TrFE)/CNT and P(VDF-TrFE)/Gr composites.

	kHz	P(VDF-TrFE)	CNT 0.02 wt%	CNT 0.05 wt%	CNT 0.1 wt%	Gr 0.02 wt%	Gr 0.05 wt%	Gr 0.1 wt%
K	0.1	9.67	10.62	10.83	11.36	12.28	12.31	12.96
	1	9.47	10.13	10.54	11.13	12.09	11.87	12.81
	10	9.23	9.88	10.17	10.79	11.77	11.38	12.54
	100	8.61	9.63	9.25	10.65	11.59	10.31	12.28
D	0.1	0.017	0.021	0.025	0.021	0.018	0.024	0.018
	1	0.017	0.023	0.027	0.023	0.021	0.025	0.021
	10	0.030	0.043	0.047	0.045	0.042	0.044	0.042
	100	0.087	0.106	0.107	0.109	0.104	0.103	0.106

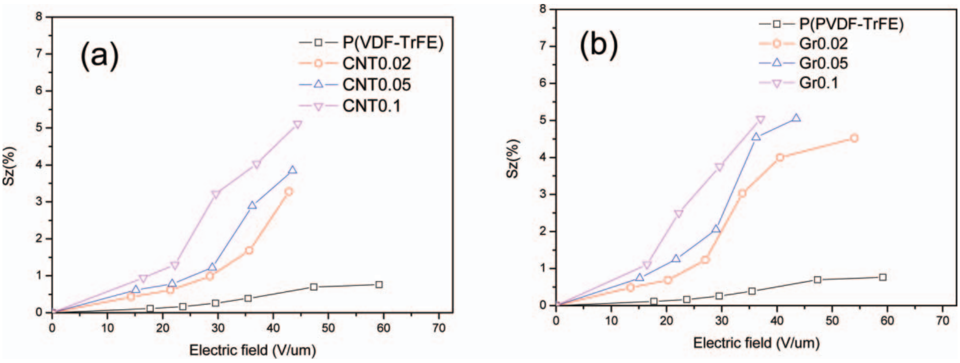
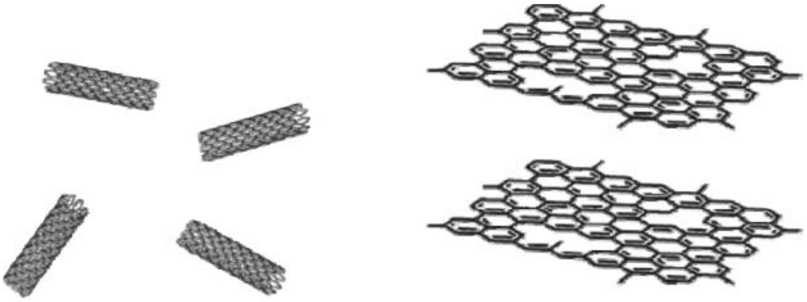


Figure 2. Electromechanical strains s_z of the (a) P(VDF-TrFE)/CNT and (b) P(VDF-TrFe)/Gr composites with various filler content as a function of an applied electric field at AC 0.1 Hz.

Figure 2 shows the thickness strains of the P(VDF-TrFE)/CNT and P(VDF-TrFE)/Gr composites at various electric fields. For the strain measurements, AC 0.1 Hz electric signal was delivered to the samples. Electric actuation strains of the composites increased quadratically with the applied AC electric field strength, which represents that PVDF composites actuated like dielectric elastomer actuators [1,2]. Although P(VDF-TrFE) had the β crystalline structure with 55% crystallinity, there was no orientational order. Therefore, the prepared P(VDF-TrFE) film and the P(VDF-TrFE) composite films had a zero d_{33} piezoelectric constant value indicating that piezoelectricity of the sample was negligible. The electrostrictive actuation strains of the composites influenced not only how much the fillers embedded but also which type filler was used. Actuation strain of the composites increased with filler content regardless of filler type. PVDF/Gr composites had larger electromechanical actuation strain s_z than P(VDF-TrFE)/CNT composites at the same filler concentration level.

In this work, we investigated P(VDF-TrFE) composites with two different carbon-based fillers: single wall carbon nanotubes (CNTs) with 1D rod shape and chemically sythesized graphene (Grs) with 2D sheet shape, as illustrated in Fig. 3. The composites showed more enhanced actuation responses than the neat P(VDF-TrFE). The actuation strains of the composites increased with the filler content. The fact that the actuation strains



(a) (b)

Figure 3. Schematic illustration of the dispersion state of (a) carbon nanotubes (CNTs) and (b) graphenes (Grs) in the composites.

of the composites were higher than those of the neat P(VDF-TrFE) was understood by the charge transport mechanism [8–14]. The presence of the fillers in the composites enhanced the ability to trap the charges because the interface between the fillers and a matrix polymer was in a high energy state and could easily trap the electrons injected from the electrodes. The charge-trapped state of the composites could achieve not only a high dielectric constant but also enhanced actuation strain. The ability of the composites to trap the charges increased with the filler content as long as the composites were electrically insulating. The actuation response of the composites was also affected by the filler type. P(VDF-TrFE)/Gr had a larger dielectric constant and s_z than P(VDF-TrFE)/CNT at the same filler concentration level. The CNTs had a tube diameter of 4 nm and a tube length of 0.5 μm (1D morphology). In contrast, the Grs had a thin platelet shape with a thickness of 1nm and a diameter of 1 μm (2D morphology), indicating that the 2D shape Gr fillers served as more effective fillers than the 1D shape CNT fillers. The difference in effectiveness might be caused by the fact that 2D shape fillers can work as more effective fillers than 1D shape fillers, because 2D fillers provided larger effective surface area than 1D shape fillers [20].

4. Conclusion

The electromechanical properties of poly (vinylidenefluoride-*co*-trifluoroethylene) (P(VDF-TrFE))/carbon nanotube (CNT) and P(VDF-TrFE)/graphene (Gr) composites have been investigated. The electromechanical thickness strain s_z of the composites increased with the filler content. In the actuation view-point of the composites, 2D platelet type Grs worked more effectively as fillers than 1D rod type CNTs. As a result, the electric actuation of the composites was influenced not only by filler concentration but also by filler type.

Acknowledgments

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References

[1] Pelrine, R., Kornbluh, R., Pei, Q., & Joseph J. (2000). *Science*, *287*, 836–389.

[2] Pelrine, R., Kornbluh, R., Joseph, J., Heydt, R., Pei, Q., & Chiba S. (2000). *Mater. Sci. Eng. C*, *11*, 89–100

[3] Shankar, R., Ghosh, T. K., & Spontak, R. J. (2007). *Soft Matter*, *3*, 1116–1129.

[4] Koo, I. M., Jung, K., Koo, J. C., Nam, J. Do., Lee, Y. K., & Choi, H. R. (2008). *IEEE Trans. Robot.*, *24*, 549–558.

[5] Kwak, J. W., Chi, H. J., Jung, K. M., Koo, J. C., Jeon, J. W., Lee, Y. K., Nam, J. D., & Choi, H. R. (2005). *J. Mech. Sci. Tech.*, *19*, 578–588.

[6] Zhang, S., Zhang, N., Huang, C., Ren, K., & Zhang, Q. (2005). *Adv. Mater.*, *17*, 1897–1901.

[7] Huang, C., & Zhang, Q. (2004). *Adv. Funct. Mater.*, *14*, 501–506.

[8] Guiffard, B., Seveyrat, L., Sebald, G., & Guyomar D. (2006). *J. of Phys. D: Appl. Phys.*, *39*, 3053–3057.

[9] Grossiord, N., Kivit, P. J. J., Loos, J., Meuldijk, J., Kytylyuk, A. V., & Vander Schoot P. (2008). *Polymer*, *49*, 2866–2872.

[10] Zou, J., Liu, L., Chen, H., Khondaker, S. I., McCullough, R. D., & Hou, Q. (2008). *Adv. Mater.*, *20*, 2055–2060.

[11] Watcharotone, S., Dmitriy, D. A., Stankovich, S., Piner, R., & Inhwa, J. (2007). *Nano Lett.*, *7*, 1888–1892.

[12] Guiffard, B., Guyomar, D., Seveyrat, L., Chowanek, Y., Bechelany, M., Cornu, D., & Miele, P. (2009). *J. of Phys. D: Appl. Phys.*, *42*, 055503.

[13] Su, J., Ting, R. Y., & Zhang, Q. M. (1997). *Appl. Phys. Lett.*, *71*, 386–388.

[14] Carbone, A., Kotowska, B. K., & Kotowski, D. (2005). *Phys. Rev. Lett.*, *95*, 236601.

[15] Hummers, W. S., & Offeman, R. E. (1958). *J. Am. Chem. Soc.*, *80*, 1339.

[16] Kovtyukhova, N. I., Ollivier, J., Martin, B. R., Mallouk, T. E., Chizhik, S. A., Buzaneva, E. V., & Gorchinskiy, A. D. (1999). *Chem. Mater.*, *11*, 771–778.

[17] Li, D., Muller, M. B., Gilje, S., Kaner, R. B., & Wallace G. G. (2008). *Nature Nanotechnology*, *3*, 101–105.

[18] Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., & Ruoff, R. S. (2007). *Carbon*, *24*, 1558–1565.

[19] Stankovich, S., Dikin, D. A., Dommett, G. H. B., Kohlhaas, K. M., Zimney, E. J., Stach, E. A., Piner, R. D., Nguyen, S. T., & Ruoff, R. S. (2006). *Nature*, *442*, 282–286.

[20] Ramanathan, T., Abdala, A. A., Stankovich, S., Dikin, D. A., Herrera-Alonso, M., Piner, R. D., Adamson, D. H., Schniepp, H. C., Chen, X., Ruoff, R. S., Nguyen, S. T., Aksay, I. A., Prudhomme, R. K., & Brinson, L. C. (2008). *Nature Nanotechnology*, *3*, 327–331.

[21] Kim, B., Park, Y. D., Kim, J., Hong, S. M., & Koo, C. M. (2010). *J. Polym. Sci. Part. B : Polym. Phys.*, *48*, 2392–2398.

[22] Shankar, R., Ghosh, T. K., & Spontak R. J. (2007). *Macromol. Rapid Commun.*, *28*, 1142–1147.