Research on automatic spraying of single-walled carbon nanotubes and detection of spraying effects

Jianwen Zhao, Jiangcheng Yu, Junyang Niu*, Yong Ge and Liwu Liu

HIT at Weihai, State Key Laboratory of Robotics and System, Song Jian Research Institute of Building 2, Wenhua Road (W), Weihai, Shandong, 264209, PR China

(Received 30 November 2013; final version received 17 March 2014)

Single-walled carbon nanotubes (SWNTs) have been introduced as compliant electrodes for dielectric elastomers (DEs) due to fault tolerance. To acquire a better electrostrictive strain and longer lifetime, it is essential to obtain a certain and uniform width of the SWNT electrode. To ensure uniform width manually, a small flux and longer time are necessary. Moreover, it is difficult to control the width of the electrode for the randomness of manual spraying. Therefore, a new type of automatic spraying process is presented in this paper. The width and homogeneity of the electrode can be easily controlled by certain parameters of the process. Two methods for detecting the homogeneity of the electrode are introduced in this paper: Measurement of surface resistance and luminosity. The coefficient of variation (CV) values detected by the two methods are virtually equal and less than 8%, which shows the feasibility of the detection method and homogeneity of automatic spraying. The speed of automatic spraying is 102 mm²/s, which is higher than that of manual spraying. The spraying process and the method used to detect homogeneity in this paper provide a reference for the relevant processes.

Keywords: single-wall carbon nanotube; automatic spraying; dielectric elastomer; homogeneity detection

1. Introduction

Acrylic elastomers have demonstrated actuated strains of over 200%, stresses of up to 7 MPa, and estimated energy densities of over 3 J/g, and such remarkable performance has attracted considerable attention [1–4]. To realize the electrostrictive strain of dielectric elastomer (DE) actuators, the sandwich structure of compliant electrode/DE/compliant electrode is applied [5]. Naturally, the research on compliant electrodes has stepped into the spotlight in regard to the characteristics of DEs. Progress has been made on different kinds of electrodes like graphite powder, carbon-filled grease, silver-filled grease [6], and single-walled carbon nanotubes (SWNTs) [7]. Among these, SWNTs are applied in the construction of DE actuators for exhibiting fault tolerance through the local degradation of SWNTs during dielectric breakdown [8,9]. To date, most researches have mainly focused on how to improve the electrostrictive strain and lifetime of DEs by the use of SWNTs [10]. Although the manufacturing process of the SWNT electrode has been studied [11], the manufacturing process of 3M VHB acrylic tapes’ SWNT electrode is still carried out

*Corresponding author. Email: niujunyang0725@gmail.com

© 2014 The Author(s). Published by Taylor & Francis.
This is an Open Access article distributed under the terms of the Creative Commons Attribution License http://creativecommons.org/licenses/by/3.0/, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The moral rights of the named author(s) have been asserted.
manually. Uncertain factors such as the homogeneity and thickness of the sprayed electrode are introduced by manual spraying, leading to longer spraying times, and thus the process cannot be controlled accurately. To provide a solution to these problems, a new type of automatic spraying process is introduced in this paper. With the prerequisite of zero damage to the SWNT structure, ultrasonic crushing equipment is used to improve the dispersibility of the SWNT. Sustainable and stable ejection from the SWNT sprinkler is achieved by this method. Finally, a continuous spraying and uniform electrode coating is realized and the area strain with fixed width is also measured in this paper.

2. Description of the automatic spraying system
The system consists of a controller (single-chip AT89C51), a powerful motor driver, and two mechanisms with translation movement, a pneumatic circuit, and a sprinkler (Figure 1).

A serpentine path is realized by the controller, stepping motor driver, and stepping motor. The sprinkler is installed on the ball screw by a clamping device. All units above are supported by standard sections and surrounded by a seal plate.

To enhance spraying, the unit describes a serpentine spraying path, with instant stopping and motion reset incorporated in the controller. Structure and design of the pneumatic circuit is shown in Figure 2.

The free end of the sprinkler is connected to the air compressor by an additional super-mist separator and solenoid valve. Similarly, the end in contact with liquid is connected to the sprinkling can, which is specifically designed according to the size of the sprinkler and the solution characteristics. The prototype is presented in Figure 3.

Figure 1. Mechanism of the new spraying machine.

Figure 2. Structure and design of the pneumatic circuit.
3. Research on the dispersibility of SWNT by ultrasonic crushing

In solution, SWNTs readily become entangled and bunched together due to the van der Waals force acting among them. From the macro perspective, SWNT powders readily aggregate into larger particles and thus during the spraying process the sprinkler is easily jammed, affecting the fluency and uniformity of spraying. Therefore, the dispersibility of SWNT solutions needs to be improved. Three types of method are commonly used: physical, chemical, and radiation [12,13]. The physical method [14] is the most suitable in regard to DE actuators, by virtue of the absence of effect on SWNT conductivity [15]. However, the most widely used physical method today is ultrasonic cleaning, but energy transfer by this method is inefficient. The level of ultrasonic energy reduced gradually when passing through multimedia to reach the SWNT solution, and dispersibility is not ideal with this method. To enhance dispersibility, the concept of ultrasonic crushing is introduced in this article.

3.1. Enhanced dispersibility of SWNT solution by ultrasonic crushing

The increasing use of powders in SWNT solutions rapidly converts these into suspensions by precipitation when poorly dispersed. The degree of precipitation is used for comparison of dispersibility between ultrasonic crushing and ultrasonic cleaning. SWNTs (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences) were dispersed in an aqueous solution (mixture of water and isopropanol 1:5 by volume) by either ultrasonic crushing or ultrasonic cleaning, yielding a solution concentration of 0.5 mg/ml. The ultrasonic cleaner was applied for 15 min under 480 W power, and ultrasonic crushing for the same time but with a pause of 3 min after running for 5 min oat200 W and 19.4 KHz. If the temperature of the solution becomes excessive, the isopropanol will evaporate rapidly. The solution was then placed in two test tubes and left to stand. Figure 4 shows dispersal of the respective solutions after having stood for 12 hours. As will be seen from this, ultrasonic crushing shows the better dispersibility.

3.2. Comparison of time to sprinkler blockage

Following addition of the dispersant, the SWNT solution will disperse efficiently but conductivity will be reduced [15]. During the spraying process, SWNT solution dispersed by physical methods with no addition of dispersant will eventually jam the sprinkler if its
inner diameter is 0.3 mm or less; time to blockage of a sprinkler is a key parameter in the spraying process.

The SWNT solution was prepared at a concentration of 1 mg/ml (water and isopropanol1:5 by volume). To clarify comparative results, the concentration used was higher than that previously and the solution divided in two. The first part was dispersed by ultrasonic crushing for 15 min (pausing for 3 min after running for 5 min), while the other was dispersed by ultrasonic cleaning for 30 min (pausing for 3 min after running for 15 min). The spraying pressure was 24 psi, and time to blockage was recorded from the start of the experiment. Three cases of failure occurred (discontinuous spraying, decreasing flux, and sprinkler clogging) during spraying, any of which could have affected the spraying results. The time when one of these failures first occurred was termed valid time, and we then calculated the average valid time. The results are shown in Table 1.

As will be seen from Table 1, the average time to blockage in ultrasonic crushing was greater than for ultrasonic cleaning, indicating that the solution dispersed by the former method can meet the demand for spraying of larger areas and wider electrodes.

Table 1. Time to sprinkler blockage during spraying.

| Discontinuity | Decrease | Blockage (s) | Minimum (s) | Average (s) |
|---------------|----------|--------------|-------------|-------------|
| (a) Ultrasonic crushing | | | | |
| 1 | / | 475 | 475 |
| 2 | / | 513 | 513 |
| 3 | / | 432 | 432 | 478.2 |
| 4 | / | 502 | 502 |
| 5 | / | 469 | 469 |
| (b) Ultrasonic cleaning | | | | |
| 1 | 100 | 120 | 150 | 100 |
| 2 | 160 | 140 | 180 | 140 |
| 3 | 256 | 215 | 280 | 215 | 131 |
| 4 | 100 | / | 116 | 100 |
| 5 | / | / | 100 | 100 |

Note: “/” denotes no occurrence.
3.3. Observation of SWNT structure

During the process of dispersion by ultrasonic crushing, the probe inserted directly into the SWNT solution leads to efficient energy transfer, but it may damage SWNT solution composition thereby affecting conductivity [16]. Thus it is necessary to observe SWNT solution composition to confirm whether it has been negatively impacted.

The SWNT solution (1 mg/ml) prepared previously was observed by scanning electron microscopy (SEM). The concentration of SWNT solution used as the electrode is generally no higher than 1 mg/ml. Images obtained by SEM are shown in Figure 5, where it will be seen that there is little variation in composition. On the other hand, the Raman spectra of the original and dispersed SWNTs were measured and compared (Figure 6). The black and red curves are Raman spectra of the original and dispersed SWNTs, respectively; the disordered carbon/graphitic carbon (D/G) peak coordinate values of the

---

Figure 5. Structure of SWNT solutions under SEM. SWNT solution dispersed by (a) ultrasonic cleaner and (b) ultrasonic crushing.

Figure 6. Raman spectra of original and dispersed SWNT solutions.
original are (1344.78, 2105.9) and (1588.62, 41,830), and those of the dispersed SWNTs are (1344.78, 2160.67) and (1591.37, 60,792.7). The D/G peak ratio of the latter is marginally less than that of the former. If the SWNT solution concentration had been reduced by ultrasonic crushing, D/G peak ratio would have been higher than the original, proof that this did not occur.

4. Comparison of the two methods in regard to electrode homogeneity detected

4.1. Detection of homogeneity by surface resistance

Homogeneity of SWNT electrodes cannot be guaranteed during manual spraying, hence the introduction of our spraying process to resolve this problem; the homogeneity of automatic SWNT electrode spraying was detected to confirm whether this process is feasible. The width, $t$ of SWNT electrodes was estimated using $t = 1/R_s s$ [17], where $R_s$ is surface resistance and $s$ the SWNT conductivity; $t$ has a proportional relation with $R_s$, so homogeneity can be analyzed by surface resistance.

SWNTs were dispersed in aqueous solution (mixture of water and isopropanol 1:5 by volume) with the aid of ultrasonic crushing for 15 min (halting for 3 min after operating for 5 min) at a concentration of 0.4 mg/ml. The operating parameters of ultrasonic crushing were 19.4 KHz, 200 W. The SWNTs were sprayed onto quadrille paper, either automatically or manually, ensuring consistency in spraying. The spraying parameters are summarized in Table 2. The parameter of pressure was optimized, with the original value ranging from 20 to 60 psi [18].

The schematic of the divided electrode during measurement of surface resistance is shown in Figure 7. The SWNT electrode was divided into five strips of $105 \times 10$ mm; a square $10 \times 10$ mm was then cut from a rectangle of $80 \times 10$ mm in the middle of each strip.

Table 2. Parameters of automatic and manual spraying.

| Spray mode      | Time (s) | Sprayed area (mm$^2$) | Pressure (psi) | Height (mm) | Flow rate (ml/min) |
|-----------------|----------|-----------------------|----------------|-------------|-------------------|
| Manual/Automatic| 90       | 105 × 70              | 24             | 100         | 1.0               |

Figure 7. Schematic of the divided electrode.
The surface resistance was measured at the spot of each square shown in Figure 7. Given that the edges of the spraying area may differ considerably from the central area, only the central 80 × 50 mm was measured. The results are shown in Figure 8.

As shown in Figure 8(a), there was no obvious distribution of manual spraying resistance, which is due to the lack of a specific motion path. The phenomenon of surface resistance in the third strip was lower than others in Figure 8(b) caused by the taper in the export of the sprinkler which sprays solution conically. The electrode coated in the third strip would be thicker because of the overlapping region between this and adjacent strips.

The characterization of thickness $x$ is equal to $1/R$. The average value was calculated from the data in Figure 8, from which we derived $\overline{x}_{\text{automatic}} = 3.1549 \times 10^{-2}/k\Omega$, $\overline{x}_{\text{manual}} = 4.0291 \times 10^{-2}/k\Omega$.

According to the standard deviation (Equation (1)) and coefficient of variation (CV) formula (Equation (2)):

$$\begin{align*}
S &= \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n - 1}} \\
\text{CV} &= \frac{S}{\overline{x}} \times 100\%
\end{align*}$$

we derive $S_{\text{automatic}} = 2.2342 \times 10^{-3}$, $S_{\text{manual}} = 1.9952 \times 10^{-2}$, $\text{CV}_{\text{automatic}} = 7.08\%$, $\text{CV}_{\text{manual}} = 49.52\%$.

The result shows that the rate of change in surface resistance with the automatic process is better than that of the manual, because $\text{CV}_{\text{automatic}}$ is less than $\text{CV}_{\text{manual}}$. Thus the homogeneity of automatic electrode spraying is better.

### 4.2. Detection of homogeneity by luminosity

There is a quantitative relationship between the luminosity of the SWNT electrode and its width. Therefore, the homogeneity of SWNT electrodes can be confirmed by detection of luminosity. A square area of the electrode (10 × 10 cm) was sprayed onto the acrylic film automatically, using the parameters for solution and spraying described in Section 4.1. Figure 9 shows the set-up for detecting the luminosity of SWNT electrodes.
The testing process comprises three steps: (1) measurement of the intensity of the light source; (2) measurement of the light intensity passing through the film without SWNTs; and (3) measurement the light intensity passing through the film with SWNTs. In the final step, measurement of the spraying area was divided into three parts, in each of which four measurement points were selected. The values obtained do not have units, because the intensity of the light measured by the instrument is a relative value. Luminosity, $T$, is calculated by

$$T = \frac{I}{I_0} \times 100\%$$

(3)

where $I$ and $I_0$ are the light intensity passing through the film and the original light intensity, respectively. The intensity of light passing through the medium is calculated by

$$I = I_0 e^{-\mu d}$$

(4)

where $e$, $\mu$, and $d$ are also the light intensity passing through the film. After performing Equation (4), $d$ can be expressed as

$$d = -\frac{1}{\mu} \ln \frac{I}{I_0} = -\frac{1}{\mu} \ln T$$

(5)

where $d$ has a proportional relationship with $\ln T$ that can be derived from Equation (5). Thus the uniformity of film thickness ($d$) can be analyzed by the CV of $\ln T$.

During measurement, light intensity at different frequencies as obtained. Luminosity of the SWNT film was calculated by the average light intensity at all frequencies; the average original light intensity and that passing through the film without SWNTs was 1725 and 1564, respectively. Table 3.

Our calculations derived $\ln T$ and its mean, standard deviation, and CV: $\ln \bar{T} = -0.126$, $S_{\ln T} = 0.00955$, $\text{CV}_{\ln T} = 7.58\%$. The luminosity of SWNT film at 12 different measurement points varied marginally, which can be inferred from the value of $\text{CV}_{\ln T}$. Hence, the thickness at these measurement points is almost identical, indicating the homogeneity of SWNT electrodes sprayed automatically.

Figure 9. Set-up for light intensity measurement: (1) optical fiber; (2) DE with SWNT sample; (3) light source; (4) spectrograph.
Table 3. Luminosity ($I_0$) calculated as 1564.

| (a) | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Light intensity | 1401 | 1365 | 1356 | 1376 | 1384 | 1379 | 1395 | 1389 | 1370 | 1381 | 1365 | 1383 |
| Luminosity $T\%$ | 89.6 | 87.3 | 86.7 | 88.1 | 88.5 | 88.2 | 89.2 | 88.8 | 87.6 | 88.3 | 87.3 | 88.4 |
| $\ln T$ | -0.110 | -0.136 | -0.143 | -0.127 | -0.122 | -0.126 | -0.114 | -0.119 | -0.132 | -0.124 | -0.136 | -0.123 |
5. Validation of the automatic spraying technique

An important index of DE-coated SWNT electrodes is area strain, and therefore we measured this parameter and corresponding SWNT electrode width. Because the homogeneity of the electrode was validated above, knowing the width of the electrode when spraying automatically, and its relation to spraying parameters, is valuable. To this end, electrode width was measured by atomic force microscopy (AFM).

5.1. Width measurement

The factors affecting the width of the SWNT electrode are the distance between the sprinkler and the film, SWNT concentration, the solution flux (controlled by a throttle valve), air pressure, and sprinkler speed of the sprinkler (Table 4).

The width of the coated SWNT electrode was 69.05 nm, as measured by AFM at the step edges (Figure 10).

Table 4. The parameters of width measurement.

| Parameter            | Concentration (mg/ml) | Pressure (psi) | Flow (ml/min) | Height (mm) | Sprinkler speed (mm/s) |
|----------------------|-----------------------|----------------|---------------|-------------|------------------------|
|                      | 0.4                   | 24             | 0.59          | 100         | 13                     |

![Figure 10. Scanning positions and measurement results.](image)
5.2. Electrostrictive strain measurement

In this part of the experiment, acrylic film was biaxially prestrained by 300%. The SWNT solution was sprayed onto the film automatically and the film was then covered by a mask incorporating a hole of 30 mm diameter. The parameters of SWNT solution and spraying were as described in Section 5.1, as was the thickness. Area strain is shown in Figure 11 for voltages applied ranging from 0 to 6 kV. The maximum area strain was 177.8% at 6 KV.

Sixteen seconds was required for automatic spraying of an area 40 × 40 mm² at a spraying speed of 102 mm²/s. To achieve the same thickness and homogeneity by manual spraying, the flux needs to be reduced and application time extended. Automatic spraying was shown to be more efficient than manual.

6. Conclusion

A novel technique of SWNT solution spraying, at a speed of 102 mm²/s, is introduced in this paper. By calculating values of luminosity and surface resistance for different parts of SWNT electrodes, the CV was 7.08% and 7.58%, respectively. All the above parameters indicate that the application of this technique will yield a uniform SWNT electrode with high spraying speed.

Ultrasonic crushing is used to improve SWNT dispersibility, and such improvement is measured by standing and blockage experimentation. SEM was also used to prove that no damage had occurred to SWNT structure.

Two methods, measurement of luminosity and surface resistance, are described to detect the homogeneity of the SWNT electrode. The CV results from these two methods are virtually identical, which proves their feasibility.

Finally, with the application of ultrasonic crushing and spraying technique, the area strain on acrylic film (VHB4910, 300% biaxially prestrained) was measured at 177.8% at 6 KV, with electrode thickness of 69.05 nm. These results show that the technique can be applied in electrode spraying.

Negative aspects found were parameters such as distance between sprinkler and film, SWNT concentration, solution flux (controlled by the throttle valve), air pressure, and sprinkler speed; these still need to be optimized to enhance the spraying technique.
Acknowledgments

This work received financial support from the National Natural Science Foundation of China. We would like to thank Professor Qibing Pei for advice on the preparation of the SWNT solution, the School of Material Engineering for providing SEM, and the Department of Physics for guidance on the detection of homogeneity.

References

[1] R. Pelrine, R. Kornbluh, and G. Kofod, High-strain actuator materials based on dielectric elastomers, Adv. Mater. 12(16) (2000), pp. 1223–1225. doi:10.1002/1521-4095(200008)12:16&lt;1223::AID–ADMA1223&gt;3.0.CO;2–2.

[2] R. Pelrine, R. Kornbluh, Q. Pei, and J. Joseph, High-speed electrically actuated elastomers with strain greater than 100%, Science 287(5454) (2000), pp. 836–839. doi:10.1126/science.287.5454.836.

[3] Q. Pei, M.A. Rosenthal, R. Pelrine, S. Stanford, and R.D. Kornbluh, Multifunctional electroelastomer roll actuators and their application for biomimetic walking robots, Smart Structures and Materials. International Society for Optics and Photonics, 2003: 281–290.

[4] J.S. Plante, L.M. Devita, and S. Dubowsky, A road to practical dielectric elastomer actuators based robotics and mechatronics: Discrete actuation. Proceedings of SPIE Electroactive Polymer Actuators and Devices, San Diego, CA. SPIE, Bellingham, WA, 2007: 652406–1.

[5] R.E. Pelrine, R.D. Kornbluh, and J.P. Joseph, Electrostriction of polymer dielectrics with compliant electrodes as a means of actuation, Sens. Actuators. A Phys. 64(1) (1998), pp. 77–85. doi:10.1016/S0924-4247(97)01657-9.

[6] P. Khodaparast, S.R. Ghaffarian, M.R. Khosrosteh, N. Yousefimehr, and D. Zamani, Electrode structures in high strain actuator technology, J. Optoelectron. Adv. Mater. 9(11) (2007), pp. 3585–3591.

[7] W. Yuan, T. Lam, J. Biggs, L. Hu, Z. Yu, S. Ha, D. Xi, M.K. Senesky, G. Grüner, and Q. Pei, New electrode materials for dielectric elastomer actuators, The 14th International Symposium on: Smart Structures and Materials & Nondestructive Evaluation and Health Monitoring. International Society for Optics and Photonics, 2007: 65240N–1–65240N–12.

[8] W. Yuan, L. Hu, S. Ha, T. Lam, G. Grüner, and Q. Pei, Self-clearable carbon nanotube electrodes for improved performance of dielectric elastomer actuators, The 15th International Symposium on: Smart Structures and Materials & Nondestructive Evaluation and Health Monitoring. International Society for Optics and Photonics, 2008: 69270P–1–69270P–12.

[9] P. Brochu and Q. Pei, Advances in dielectric elastomers for actuators and artificial muscles, Macromol. Rapid. Commun. 31(1) (2010), pp. 10–36. doi:10.1002/marc.200900425.

[10] W. Yuan, P. Brochu, S.M. Ha, and Q. Pei, Dielectric oil coated single-walled carbon nanotube electrodes for stable, large-strain actuation with dielectric elastomers, Sens. Actuators. A Phys. 155(2) (2009), pp. 278–284. doi:10.1016/j.sna.2009.09.003.

[11] Y. Zhou, L. Hu, and G. Gruner, A method of printing carbon nanotube thin films, Appl. Phys. Lett. 88(12) (2006), pp. 123109–123109-3. doi:10.1063/1.2187945.

[12] N. Pierard, A. Fonseca, Z. Konya, I. Willems, G. Van Tendeloo, and J.B. Nagy, Production of short carbon nanotubes with open tips by ball milling, Chem. Phys. Lett. 335(1–2) (2001), pp. 1–8. doi:10.1016/S0009-2614(01)00004-5.

[13] C.A. Dyke and J.M. Tour, Covalent functionalization of single-walled carbon nanotubes for materials applications, J. Phys. Chem. A 108(51) (2004), pp. 11151–11159. doi:10.1021/jp046274g.

[14] C. Ménard-Moyon, N. Izard, E. Doris, and C. Mioskowski, Separation of semiconducting from metallic carbon nanotubes by selective functionalization with azomethine ylides, J. Am. Chem. Soc. 128(20) (2006), pp. 6552–6553. doi:10.1021/ja060802f.

[15] E. Bekyarova, M.E. Itkis, N. Cabrera, B. Zhao, A. Yu, J. Gao, and R.C. Haddon, Electronic properties of single-walled carbon nanotube networks, J. Am. Chem. Soc. 127(16) (2005), pp. 5990–5995. doi:10.1021/ja0431531.

[16] T. Sina, Y. Xiaohong, and D. Jianwen, The effects of both length and tube-diameter on the conductance of single-walled carbon nanotubes, Acta. Phys. Sin. 54(1) (2005), pp. 333–337.
[17] W. Yuan, L.B. Hu, Z.B. Yu, T. Lam, J. Biggs, S. Ha, D. Xi, B. Chen, M. Senesky, G. Grüner, and Q. Pei, *Fault-tolerant dielectric elastomer actuators using single-walled carbon nanotube electrodes*, Adv. Mater. 20(3) (2008), pp. 621–625. doi:10.1002/adma.200701018.

[18] O. Assad, A.M. Leshansky, B. Wang, T. Stelzner, S. Christiansen, and H. Haick, *Spray-coating route for highly aligned and large-scale arrays of nanowires*, ACS Nano 6(6) (2012), pp. 4702–4712. doi:10.1021/nn204513y.