Chapter 3
Carbon Nanotube (CNT) Elastomers for Sensing Applications: A Narrative Review

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Abstract Elastomers are traditionally considered materials with low tensile strength and minimal electrical conductivity. Carbon nanotubes (CNT) are classified as fullerenes, or carbon-based materials forming a molecular mesh, that assume a cylindrical shape and display remarkable properties, such as high tensile strength and enhanced electrical conductivity as compared to other carbon allotropes. Elastomers doped with carbon nanotubes form CNT elastomers, which act as semi-conductors and can be formulated to exhibit many useful characteristics for the design of various sensors, such as strain gages. While CNT elastomers have been studied for more than 20 years, there are relatively few, if any, commercial sensor products utilizing this innovative technology. In this chapter, we survey selected portions of the CNT literature, explore the operation and characteristics of CNT elastomers, and consider some CNT elastomer requirements of potential interest for the design of sensors.

Keywords Carbon nanotubes · CNT · Elastomer · Strain gauge · Strain gage

3.1 Polymers

Polymers are a generic term for any molecule, organic or synthetic, composed of repeating subunits. Formed by a polymerization process, or the chemical reactions used to join constituent monomers into a polymer chain, polymers play important roles in modern daily life. For example, plastics are synthetic (or sometimes semi-organic) polymers composed of hydrocarbon monomers [1]. Even deoxyribonucleic acids (or DNA) that forms the basis of human life are polymers comprised of nucleotide monomers [2]. In their unprocessed or raw state, polymers often assume the shape of long, flexible strings, much like a cooked spaghetti noodle [3], and are not particularly useful in the construction of practical products. Further processing of raw polymers, such as by introducing small amounts of selected additives, can change the bulk characteristics of those polymers into useful engineering materials.

3.2 Elastomers

Elastomers are a class of polymers characterized by occasional cross-linking of the long-chain polymers, such as by covalent cross-linking [4]. The stiffness of an elastomer is governed by the number of polymer cross-links, such as increasing cross-link density results in stiffer elastomers [5]. The cross-linking process can include the addition of a cross-link promoter (or "cross-linker") to the raw polymer and then exposing the combined materials to either a source of energy, such as gamma radiation, or chemical activation, such as by mixing the combined materials with peroxide [6]. The elasticity of an elastomeric material is characterized by its ability to "move" or otherwise reconfigure its amorphous structure under an applied load, yet return to its original structural configuration after the load is removed due to the "memory" of the material introduced by the cross-linking process [7].

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3.3 Compounding

The process of compounding can further refine the properties of an elastomer through the addition of fillers or additives that can impart special characteristics to the elastomer, such as color, impermeability, or oil resistance [8]. Fillers can also be added to “reinforce” an elastomer, such as to improve tensile strength, abrasion resistance, and extension moduli. For example, carbon black, a paracrystalline form of carbon with a high surface-area-to-volume ratio [9], is a common elastomer reinforcement filler [10]. Owing to surface chemistry, where a large percentage of carbon atoms are available to interact with the polymer matrix, carbon black is hypothesized to increase elastomer tensile strength through physical adsorption with the elastomeric polymer and covalent bonding at cross-linking points [11]. Another example of a carbon-based elastomer filler is the carbon nanotube (or CNT).

3.4 Carbon Nanotubes (CNT)

Originally synthesized and identified in 1952 [12] and subsequently “rediscovered” in 1991 [13], the CNT is a fullerene or a carbon-based material forming a molecular mesh that assumes a cylindrical shape [14]. See Fig. 3.1.

Physically, the diameter of a CNT can vary in the range of about 0.4–40 nanometers (nm) with lengths from 0.14 nm to 55.5 cm [16]. See Fig. 3.2. CNT display unusual tensile strength (50+ GPa) as compared to carbon steel (540 MPa) [17]. Single-walled CNT are predicted to have an electrical resistance of ∼6 kΩ independent of length and diameter [17].

3.5 CNT Elastomers

Apart from their enhanced mechanical properties, elastomers doped with CNT fillers also exhibit advantageous electrical properties. While elastomers are typically considered an insulating material unable to conduct electrical charge, CNT-doped elastomers act as conducting materials, capable of transmitting a current through the elastomer in response to an applied

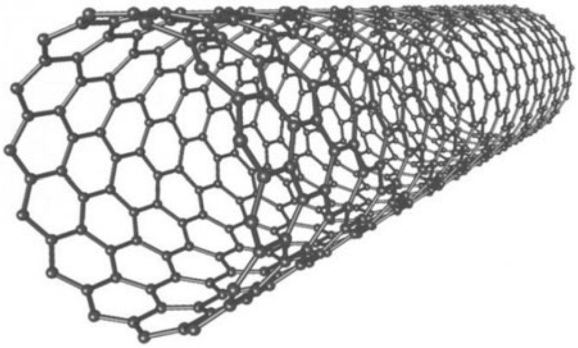

Fig. 3.1 Molecular structure of a single-walled carbon nanotube (SWCNT) [15]

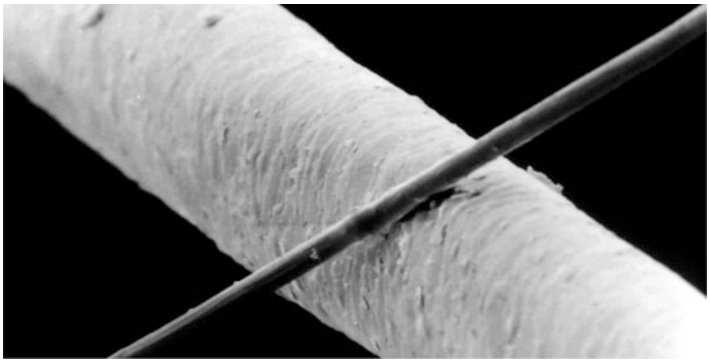

Fig. 3.2 Scale of a CNT (thin tube) compared to a human hair (thick tube; diameter = ∼50 nm) [18]

voltage [19]. Electrical conductivity is induced as the CNT filler is dispersed throughout the insulating elastomer at a density sufficient to create a conducting network through the elastomer, such as by direct contact of CNTs creating a conduction path or by CNTs in close proximity to each other in a process known as "tunneling" [20]. In an example, CNT elastomers can be formed into the shape of a sensor, such as a resistance strain gauge. As load is applied to the CNT elastomer strain gauge, the elastomer material deforms, interrupting current transmission paths by "breaking" connections between conducting CNT in the elastomer matrix, increasing the electrical resistance of the strain gauge [21, 22]. As the load is released, the elastic nature of the CNT elastomer will cause the gauge to return to its undeformed state, reestablishing the electrical CNT connections and reducing electrical resistance of the strain gauge.

3.6 Factors Affecting CNT Elastomer Conductivity

Figures 3.3 and 3.4 illustrate the effect of CNT concentration on conductivity within an elastomer matrix [23]. In illustration (a) of Fig. 3.3, a low concentration of well-dispersed CNT does not allow for contact between CNT particles, resulting in low electrical conductivity shown in Fig. 3.4 at location a. In illustration (b) of Fig. 3.3, increased CNT concentration brings CNT particles into closer proximity and promotes "tunneling" effects [21], where electrical current can pass without physical connection between CNT particles and increases conductivity as shown in Fig. 3.4 at location b. In illustration (c) of Fig. 3.3, increased CNT concentration allows CNT particles to contact one another and provides a continuous electrical pathway through the elastomer (shown as red CNT particles in illustration (c)) to achieve the so-called percolation threshold shown in Fig. 3.4 at location c. Note that the percolation threshold can be considered the CNT concentration that will lead to an abrupt increase in electrical conductivity (or correspondingly, a sharp decrease in electrical resistance) through the elastomer. In illustration (d) of Fig. 3.3, further increases in CNT concentration lead to multiple flanking electrical paths (shown as blue CNT particles in illustration (d)) and ultimately, electrical saturation of the elastomer shown in Fig. 3.4 at location d.

In addition to CNT concentration, volumetric distribution of the CNT filler in the elastomer matrix has been reported to affect conductivity [24]. Due at least in part to surface chemistry, CNT particles tend to agglomerate prior to elastomeric compounding to form "balls" or clumps of CNT [25] thought to be drawn together by ionic bonding. In general, compounding techniques that generate a more even dispersion of CNT particles through the elastomer matrix will result in a larger number of conduction paths to increase CNT elastomer conductivity and potentially lower the amount of CNT filler required to achieve the percolation threshold.

The use of CNT elastomers in sensor applications have been thoroughly explored in the literature. For example, reference to pressure sensing applications include work on "smart" skin, such as for haptic sensing applications [26], and sandwich-type piezoresistive pressure sensors [27], such as for measurement of mechanical loads. Similarly, considerable effort has been directed to strain sensing applications including sensors for human motion detection [28–30], roadway assessment [31–33], and general strain measurement purposes [34–36]. Many of these studies report excellent results, including substantially

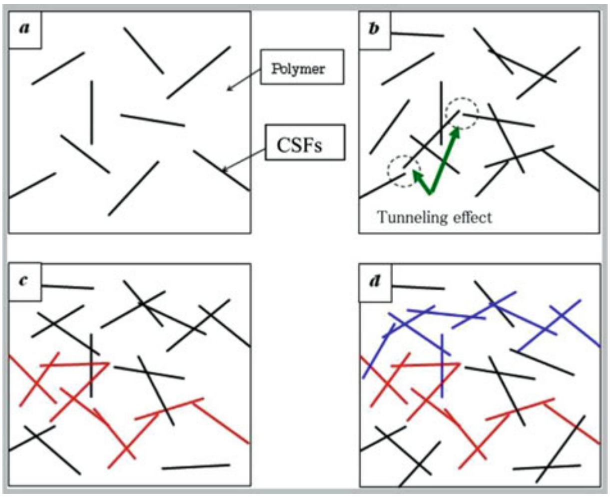

Fig. 3.3 (left) CNT concentration in the elastomer matrix can affect conductivity [23]

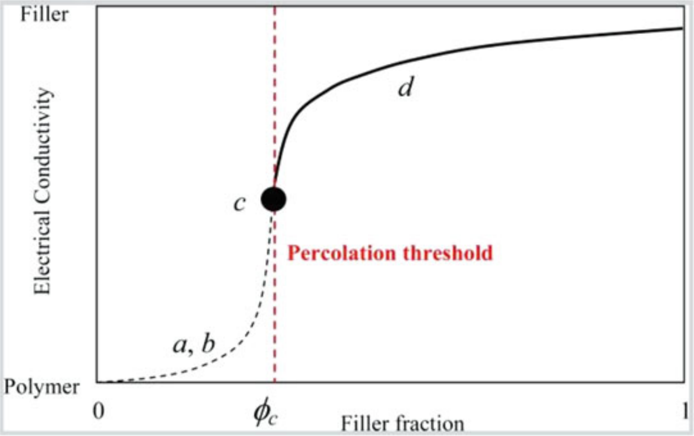

Fig. 3.4 (right) A graph of filler fraction to electrical conductivity [23]

linear response and little to no hysteresis characteristics [37]. However, even with the benefit of more than 30 years of academic research and discussion, the authors are unable to find any commercial products utilizing CNT elastomers.

At least two issues have been suggested to explain the lack of widespread CNT elastomer adoption – stability and repeatability [21]. Stability refers to fluctuations in sensor resistance not associated with mechanical loading whereas repeatability is characterized as the "repeatable resistance-strain performance" of a sensor [21]. Similar to their foil strain gauge counterparts, CNT strain gauges can experience environmental factors that affect the stability of resistance measurements, such as temperature sensitivity [38] and humidity [39], as well as factors unique to CNT elastomers, such as chemical effects [40] and particle size effects [41]. One source of undesirable resistance repeatability is manifested with the presence of hysteresis [42], which has been suggested to indicate the degradation of the CNT elastomer while in use. It is hypothesized the as least some of the challenges related to stability and repeatability can be addressed with improved CNT elastomer processing.

3.7 Factors Affecting CNT Elastomer Stability and Repeatability

There are several factors that can be controlled, or otherwise influenced, at the elastomer compounding stage that may improve the stability and repeatability of CNT elastomer response.

3.7.1 Polymer Matrix

Proper selection of the polymer matrix optimized for a particular characteristic might reduce stability challenges associated with CNT elastomers. Viscosity of the polymer matrix might be selected based upon the type of compounding force used [23]. For example, relatively inviscid polymers can be selected where a high-speed shear mixer is intended for compounding, whereas relatively viscous polymers might be better suited for sonication dispersion. Similarly, selection of a polymer with an appropriate molecular weight can be considered to facilitate CNT tunneling in polymers with low weight-faction CNT loads. Further, compounding fillers can be selected to control moisture content [41], which has been shown to cause considerable variation in the measured resistance of unstrained structural cement applications [43].

3.7.2 CNT Particles

Several aspects of CNT particles can affect the stability and repeatability characteristics of CNT elastomers. The size, shape, and aspect ratio of CNT particles have been noted as variables that can affect the measured resistance of a CNT elastomer [23]. Molecular functionalization, or the process of adding new capabilities or properties to a material by changing the surface chemistry of the material, can be applied to CNT, such as to improve CNT dispersion in an elastomer matrix [13, 44] or improve conductivity [45]. Further, the type of CNT used, such as single-walled carbon nanotube (SWCNT), multi-walled carbon nanotube (MWCNT), or thin-walled carbon nanotubes (TWCNT), can affect CNT elastomer performance. For example, several studies have suggested CNT elastomers can demonstrate piezo-electric characteristics with the use of MWCNT particles compounded into an elastomer matrix [46, 47].

3.7.3 Compounding Variables

The methods of CNT dispersion can also play a significant role in the stability and repeatability of CNT elastomers. CNT loading of an elastomer, or the amount of CNT particles required to achieve a percolation threshold, can adjust the conductivity of a CNT elastomer. For example, increasing CNT loading can potentially improve overall repeatability by increasing the volume fraction of CNT in contact with the elastomer matrix. However, additional CNT loading will also increase bulk stiffness of the elastomer, such as to reduce sensitivity of the CNT elastomer to displacement. The mechanical compounding process can also affect stability and repeatability. For example, two common compounding techniques, shear mixing and sonication, induce CNT dispersion in substantially different ways. The effects of mixing speed, mixing time, and other variables have been reported to impact the electrical properties of the CNT elastomer [23]. Curiously, curing temperature and mixing conditions have also been identified as significant variables influencing the formation of the CNT conducting network [48], which could affect the stability and repeatability of CNT elastomer materials.

3.8 Conclusions

CNT elastomers are materials with interesting electrical properties that offer many opportunities for sensor applications. However, despite extensive research and a long history of publications, few (if any) commercial products utilize CNT elastomers as a component in their construction. Two characteristics of CNT elastomers, the stability of electrical resistance response and the repeatability of electrical resistance response in elastomers subjected to dynamic loading, have been identified as potentially limiting factors to the use of CNT elastomers in sensor applications. It is hypothesized that improved control of the CNT elastomer compounding process could play a role in increasing the stability and repeatability of CNT elastomer material response.

References

1. https://omicoplastics.com/blog/plastics-polymers-difference/. Accessed Aug 2022
2. https://www.ebi.ac.uk/training/online/courses/biomacromolecular-structures/dna/. Accessed Aug 2022
3. https://www.cmu.edu/gelfand/lgc-educational-media/polymers/what-is-polymer/index.html#:~:text=Polymers%20have%20interesting%20behavior%20and,in%20a%20bowl%20of%20pasta. Accessed Aug 2022
4. https://www.osborneindustries.com/news/elastomers-vs-polymers/#:~:text=An%20elastomer%20is%20made%20from,elongation%2C%20flexibility%2C%20and%20elasticity. Accessed Aug 2022
5. https://en.wikipedia.org/wiki/Cross-link. Accessed Aug 2022
6. https://www.mddionline.com/news/cross-linking-thermoplastic-elastomers-improved-product-performance. Accessed Aug 2022
7. Özdemir, T.: Chapter 5: Elastomeric micro- and nanocomposites for neutron shielding. In: Micro and nanostructured composite materials for neutron shielding applications, pp. 125–137 (2020). https://doi.org/10.1016/B978-0-12-819459-1.00005-2
8. Pajarito, B.: Differentiation of non-black fillers in rubber composites using linear discriminant analysis of principal components. J. Sci. Eng. Compos. Mater. **26**, 282–291 (2019)
9. https://en.wikipedia.org/wiki/Carbon_black. Accessed Sept 2022
10. Rothon, R.: Particulate fillers in elastomers. In: Polymers and Polymeric Composites: A Reference Series Book Series, pp. 125–146 (2017)
11. Robertson, C., et al.: Nature of carbon black reinforcement of rubber. Perspect. Orig. Polym. Nanocompos. **13**(4), 538 (2021)
12. Katz, E.: Credit to Pioneering Work on Carbon Nanotubes. https://arxiv.org/ftp/arxiv/papers/2105/2105.03658.pdf. Accessed Oct 2022
13. Wong, K.-K., et al.: Mechanical and thermal behavior of a polymer composite reinforced with functionalized carbon nanotubes. Key Eng. Mater. **334–335**, 705–708 (2007)
14. Gomez-Bualdron, D., et al.: Chapter 5: Carbon nanotubes: engineering biomedical applications. In: Progress in Molecular Biology and Translational Science, vol. 104, pp. 175–245 (2011). https://doi.org/10.1016/b978-0-12-416020-0.00005-x
15. https://innovationsgesellschaft.ch/en/evaluation-of-the-health-effects-of-carbon-nanotubes/. Accessed July 2022
16. https://en.wikipedia.org/wiki/Carbon_nanotube. Accessed Aug 2022

17. Kang, I., et al.: Introduction to carbon nanotube and nanofiber smart materials. Compos. Part B. **37**(6), 382–394 (2006)
18. https://www.reddit.com/r/pics/comments/5whh0p/a_single_carbon_nanotube_on_a_human_hair_for_scale/. Accessed Aug 2022
19. Mensah, B., et al.: Carbon nanotube-reinforced elastomeric nanocomposites: a review. Int. J. Smart Nano Mater. **6**(4), 211–238 (2015)
20. Prabhakar, R., et al.: Tunneling-limited thermoelectric transport in carbon nanotube networks embedded in poly(dimethylsiloxane) elastomer. ACS Appl. Energy Mater. **2**(4), 2419–2426 (2019)
21. Obitayo, W., et al.: A review: carbon nanotube-based Piezoresistive strain sensors. J. Sens. (2012). https://doi.org/10.1155/2012/652438
22. Kim, T.G., et al.: Electrically conductive silicone-based nanocomposites incorporated with carbon nanotubes and silver nanowires for stretchable electrodes. ACS Omega. **6**(47), 31876–31890 (2021)
23. Alamusi, et al.: Piezoresistive strain sensors made from carbon nanotubes based polymer nanocomposites. Sensors (Basel). **11**(11), 10691–10723 (2011)
24. Liu, C.-X., et al.: Improved dispersion of carbon nanotubes in polymers at high concentrations. Nanomaterials (Basel). **2**(4), 329–347 (2012)
25. Hnog, J.S.: Extension-induced dispersion of multi-walled carbon nanotube in non-Newtonian fluid. J. Rheol. **51**, 5 (2007)
26. He, Y., et al.: A breathable, sensitive and wearable piezoresistive sensor based on hierarchical micro-porous PU@CNT films for long-term health monitoring. Compos. Sci. Technol. **200**, 108419 (2020)
27. Ali, A.: Pressure sensitive sensors based on carbon nanotubes, graphene, and its composites. J. Nanomater. **2018** (2018). https://doi.org/10.1155/2018/9592610
28. Demidenko, N., et al.: Flexible strain-sensitive silicone-CNT sensor for human motion detection. Bioengineering (Basel). **9**(1), 36 (2022)
29. Shu, W.-B., et al.: Direct ink writing of graphene/Cnt/silicone composite strain sensor with near-zero temperature coefficient of resistance. J. Mater. Chem. C. (2022). https://doi.org/10.2139/ssrn.4022067
30. Lu, Y., et al.: Recent developments in bio-monitoring via advanced polymer nanocomposite-based wearable strain sensors. Biosens. Bioelectron. **123**, 167–177 (2019)
31. Xin, X., et al.: The innovative self-sensing strain sensor for asphalt pavement structure: substitutability and synergy effects of graphene platelets with carbon nanotubes in epoxy composites. Front. Mater. (2022). https://doi.org/10.3389/fmats.2022.824364
32. Yu, X., et al.: Carbon Nanotube Based Self-Sensing Concrete for Pavement Structural Health Monitoring. https://rosap.ntl.bts.gov/view/dot/40249
33. Camacho-Ballesta, C., et al.: Performance of cement-based sensors with CNT for strain sensing. Adv. Cem. Res. **28**(4), 1–11 (2015)
34. Thompson, B., et al.: Aerosol printed carbon nanotube strain sensor. Proc. SPIE Int. Soc. Opt. Eng. (2012). https://doi.org/10.1117/12.914964
35. Lee, D., et al.: Microfabrication and characterization of spray-coated single-wall carbon nanotube film strain gauges. Nanotechnology. **22** (2011). https://doi.org/10.1088/0957-4484/22/45/455301
36. Kang, I., et al.: Introduction to carbon nanotube and nanofiber smart materials. Compos. Part B Eng. **37**(6), 382–394 (2006)
37. Cai, L., et al.: Super-stretchable, transparent carbon nanotube-based capacitive strain sensors for human motion detection. Sci. Rep. (2013). https://doi.org/10.1038/srep03048
38. Jang, S.-H., et al.: Carbon nanotube-reinforced smart composites for sensing freezing temperature and deicing by self-heating. Nanomater. Nanotechnol. (2018). https://doi.org/10.1177/1847980418776473
39. Saleem, M., et al.: Humidity sensing properties of CNT–OD–VETP nanocomposite films. Physica E. **43**(1), 28–32 (2010)
40. Li, X., et al.: Multiwalled carbon nanotube film for strain sensing. Nanotechnology. **19**(4), 045501 (2008)
41. Loh, K., et al.: Multifunctional layer-by-layer carbon nanotube–polyelectrolyte thin films for strain and corrosion sensing. Smart Mater. Struct. **16**(2), 429 (2007)
42. DeFocatiis, D., et al.: Electromechanical hysteresis in filled elastomers. In: Constitutive Models for Rubber VII, Proceedings of the 7th European Conference on Constitutive Models for Rubber. Taylor & Francis (2011). https://doi.org/10.1201/b11687-45
43. Teng, F., et al.: Piezoresistive/piezoelectric intrinsic sensing properties of carbon nanotube cement-based smart composite and its electromechanical sensing mechanisms: a review. Nanotechnol. Rev. (2021). https://doi.org/10.1515/ntrev-2021-0112
44. Dubey, R., et al.: Functionalized carbon nanotubes: synthesis, properties and applications in water purification, drug delivery, and material and biomedical sciences. Nanoscale Adv. (2021). https://doi.org/10.1039/D1NA00293G
45. Jeon, I.-Y., et al.: Functionalization of carbon nanotubes. In: Carbon Nanotubes – Polymer Nanocomposites (2011). https://doi.org/10.5772/18396
46. Il'ina, M., et al.: Piezoelectric response of multi-walled carbon nanotubes. Materials. (2018). https://doi.org/10.3390/ma11040638
47. Il'ina, M., et al.: Analysis of the piezoelectric properties of aligned multi-walled carbon nanotubes. Nanomaterials (Basel). (2021). https://doi.org/10.3390/nano11112912
48. Hu, N., et al.: Effect of fabrication process on electrical properties of polymer/multi-wall carbon nanotube nanocomposites. Compos. A: Appl. Sci. Manuf. **39**(5), 893–903 (2008)