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Composites of Functionalized Multi-Walled Carbon Nanotube and Sodium Alginate for Tactile Sensing Applications

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Abstract: Flexible tactile sensors are foreseen to be extensively used soon in wearable devices. Various materials in flexible sensor fabrication offer sensing properties with multiple capabilities. The materials, including nanocomposites, have a crucial research area for flexible tactile sensors. While the nanocomposites' electrical properties mainly depend on the nanofillers, the mechanical properties are determined by the polymer component. Carbon nanotubes (CNTs) are one of the most promising materials among nanofillers due to their high electrical conductivity, thermal stability, and durability. However, CNTs should be processed to increase the binding capacity with the polymer structure. In this study, the nanocomposite used for sensor manufacturing consists of acid-functionalized CNTs and sodium alginate as the nanofiller and the polymer material, respectively. The sensor material was cross-linked using calcium chloride, and glycerin was involved in the sensor fabrication to check the effect on the sensing and flexibility. Also, it is critical to note that sodium alginate and glycerin are biocompatible and biodegradable substances. In the scope of the study, the impedance changes of the fabricated tactile sensors were examined in the 100 Hz–10 MHz frequency range and the equivalent circuits of the sensors were created. Besides, the impedance changes were obtained when the alternating forces were applied to the sensors. The results show that the frequency responses of the sensors differ from each other in different frequency ranges. Also, each sensor has different sensing mechanisms in specific frequency ranges, and the sensor, including glycerin, has higher flexibility but less sensitivity.

Keywords: tactile sensor; functionalized-CNT; impedance sensor; sodium alginate

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1. Introduction

Composite materials are gaining attention in flexible tactile sensor fabrication. They generally consist of a non-conductive polymer matrix and conductive filler element. The aim is to assemble the mechanical properties of the polymer and the electrical features of the nanofiller component. In this way, the composites are expected to have superior characteristics compared to traditional sensor materials. It is possible having functional sensors using the composites [1]. While polymers cover elastomers and hydrogels [2,3], conductive fillers include carbon-based nanoparticles and metallic nanoparticles [1,4]. Among the carbon-based nanoparticles, CNTs have been studied and examined broadly due to their mechanical, thermal, and electrical properties [1,5,6]. However, adding even a small amount of CNTs to the polymer may cause a more rigid structure [1,6]. Therefore, to obtain a more flexible structure for a flexible sensor, some plasticizers can be included in the composite fabrication. Glycerol decreases the interactions between neighboring gel chains and acts as a plasticizer. In this way, it contributes to elasticity and mechanical properties of hydrogels [7,8], and it is a biocompatible component. Therefore, it is incorporated into the sensor fabrication. In this study, two different sensors were fabricated using a nanocomposite. The nanocomposite consists of acid-functionalized CNT and sodium alginate. To check the effect on flexibility, glycerin was contained in one of the sensors. Because of that, it also affects the sensitivity, the sensitivities of the sensors were compared as well. Alternating forces were applied to the sensors, and the impedances were measured for this purpose. Also, the AC behaviors of the sensors were examined through equivalent circuits. It was interpreted in the range of 100 Hz and 10 MHz. The results show that the frequency response of the sensors differs from each other, and they have different equivalent circuits.

2. Materials and Sensor Fabrication

The sensors were fabricated using CNTs (MWCNT, 10–20 nm, Nanografi), sodium alginate (Alfasol), and glycerin (Dermolife, medical grade). CNTs were functionalized using nitric acid and sulfuric acid according to the method proposed in [9]. First of all, 2 gr of sodium alginate was dissolved in 150 ml of deionized water. The solution was prepared at 80 °C and stirred at 600 rpm for 3 h to obtain a homogenous solution. Then, 40 mL of sodium alginate (SA) solution was taken to two separate vessels and about 4% fCNT was added to both of them gradually. One of the prepared solutions was crosslinked by calcium chloride. Glycerin was added to the other solution and then cross-linked in the same way. The hardened structures were kept for 24 h at room temperature before the measurements.

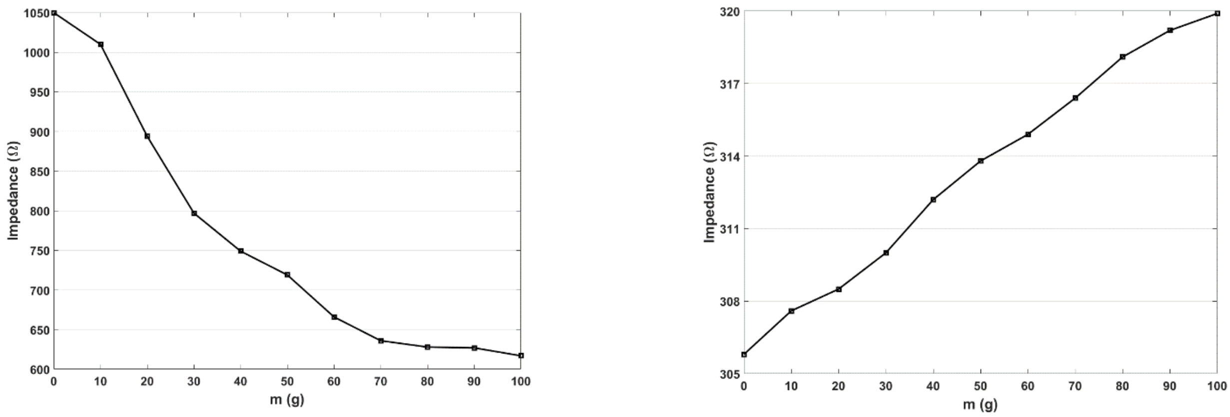
3. Results

3.1. Pressure Responses of the Sensors

The sensors were tested using an automated force stage, and the impedances were recorded using an LCR meter (Keithley U1733C). Figure 1a shows the pressure response of the sensor to applied forces without glycerin. The impedance of the sensor decreases with the increasing force magnitudes. When the pressure is applied, CNT particles get closer, and more conductive paths are formed [10,11]. It results in a decrease in the impedance. Figure 1b shows the impedance change with pressure applied to the glycerin-containing sensor. It is seen that as the force arises, the impedance ascends as well. This phenomenon originates from the disconnection and microcracks between CNTs raised [10]. The sensitivity of a pressure sensor can be calculated by Equation (1), where Z and F represent the impedance and the force, respectively.

$$S = \frac{\Delta Z / Z_0}{\Delta F} \quad (1)$$

According to Equation (1), while the sensitivity of the sensor in Figure 1a is 0.421/N, the sensitivity of the sensor in Figure 1b is 0.045/N. The sensitivity values show that the sensor not having glycerin is more sensitive. It may have been caused by the glycerin leading to the partial agglomeration of CNTs. Although the glycerin sensor is less sensitive, it is more flexible than the other. Because glycerin acts as a plasticizer and it affects the mechanical structure and elasticity of the sensor.

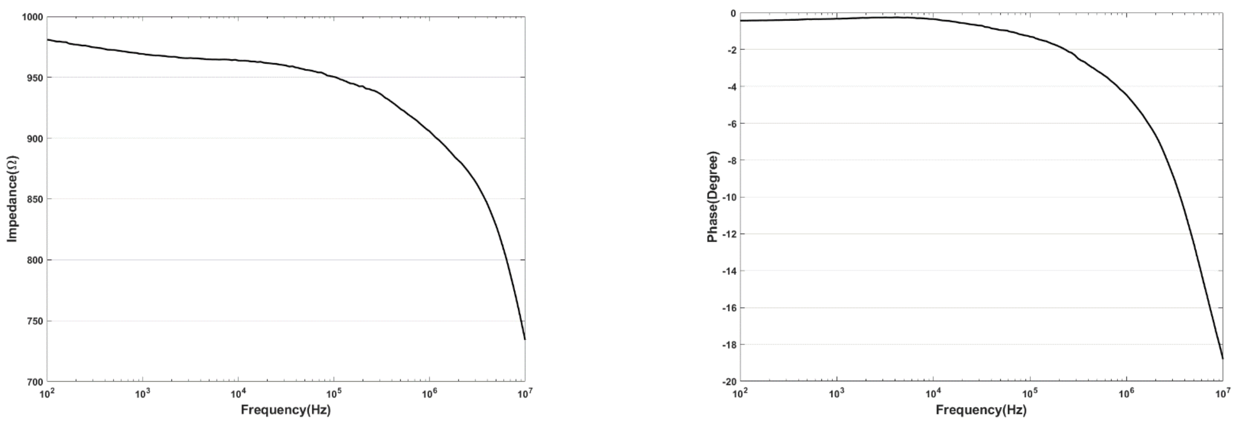


(**a**) (**b**)

Figure 1. The force—impedance relation for the sensor consisting of fCNT and SA composite (**a**) not including glycerin (**b**) including glycerin.

3.2. AC Behaviors of the Sensors

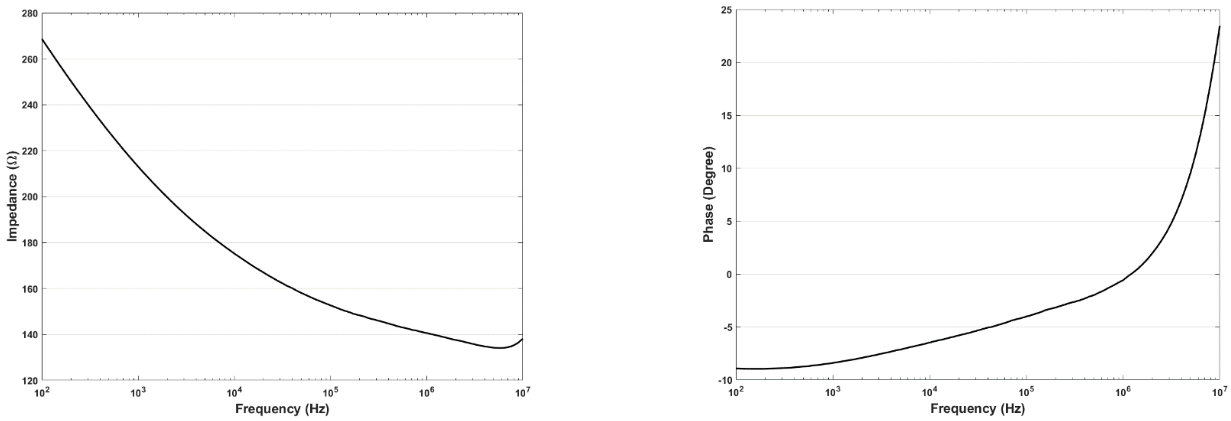
The impedance measurements of fabricated sensors were taken to evaluate the resistive and capacitive effects together. Because the impedance is closely related to the frequency, the impedance response was investigated in a certain frequency range. The AC behaviors of the sensors were examined using an impedance analyzer (Analog Discovery, Digilent) in the range of 100 Hz and 10 MHz. Figures 2 and 3 show the impedance amplitudes and phase angles of the sensors in the determined frequency range. While the data in Figure 2 belong to the sensor without glycerin, the data in Figure 3 belong to the sensor including glycerin. Figure 2a shows the impedance magnitude versus frequency. As the frequency increases, the impedance decreases and the phase angle decreases as well after almost 10kHz. It can be said that the working mechanism of the sensor is resistive until nearly 10kHz. After the frequency of 10 kHz, the sensor is getting closer to a capacitive sensing mechanism. Because CNTs in the composite can produce a great number of micro capacitors [5].



(**a**) (**b**)

Figure 2. For the sensor not including glycerin (**a**) Impedance amplitude versus frequency relation (**b**) Phase angle versus frequency relation.

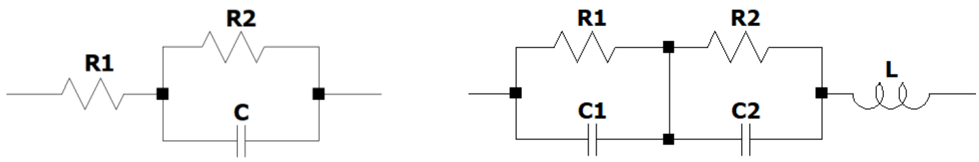
Figure 3a shows that the impedance declines as the frequency increases. The decrease is sharper than Figure 2a, and Figure 3b shows the phase change with the frequency. The phase is negative until 1 MHz, and it turns positive after 1Mhz. Whereas the working mechanism of the sensor is resistive until 1 MHz, the inductive effect appears after that point. The inductive effect may be sourced from the curling of CNTs in the composite [12].



(**a**) (**b**)

Figure 3. For the sensor including glycerin (**a**) Impedance amplitude versus frequency relation (**b**) Phase angle versus frequency relation.

Impedance and phase information were used to constitute the equivalent circuits. The proposed circuits for the sensors are given in Figure 4.



(**a**) (**b**)

Figure 4. Equivalent circuit of the sensor (**a**) not including glycerin (**b**) including glycerin.

$$|Z| = R_1 + \frac{1}{\frac{1}{jWC} + \frac{1}{R_2}} \quad (2)$$

Figure 4a shows the equivalent circuit of the first sensor that does not include glycerin, and Figure 4b shows the equivalent circuit of the second sensor that includes glycerin. The first sensor can be modeled with RC parallel circuit, and the magnitude of the impedance is given in Equation 2. The equation states that the equivalent impedance consists of a resistor in series with a parallel connected resistor and capacitor. The equivalent circuit of the second sensor includes an inductor with parallel RC components. Its impedance magnitude can be found in Equation 3. The Equation 3 expresses that the equivalent impedance consists of an inductor in series with parallel connected resistors and capacitors. Though some inductive effects may be incorporated in the first sensor's circuit, it can be neglected due to being very small, and it has almost no effect on the frequency spectra. However, the magnitude of the inductance in the second sensor's circuit cannot be neglected because its effect is obvious on the frequency response.

$$|Z| = \frac{1}{\frac{1}{R_1} + \frac{1}{jWC_1}} + \frac{1}{\frac{1}{R_2} + \frac{1}{jWC_2}} + jWL \quad (3)$$

4. Conclusions

This study focuses on the sensitivity and frequency behavior of two different sensors. The difference between fabricated sensors sources from the glycerin. Glycerin is a plasticizer, and it directly affects the structure to which it is added. Besides the mechanical structure, it also changes the sensitivity of the sensor. The measurement results show that the sensor including glycerin is more flexible but less sensitive. While the sensitivity of the sensor including glycerin is 0.045/N, the sensor not including glycerin is 0.421/N. In addition, the frequency spectra of the sensors were examined in the range of 100 Hz–10 MHz, and the equivalent circuits were constructed. Whereas the equivalent circuit of the sensor without glycerin consists of parallel RC components, the equivalent circuit of the sensor with glycerin has an inductor element. The studies from the literature propose that CNTs agglomeration leads to such an inductive effect [12].

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