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# Optimization of Manufacturing Conditions of Pressure-Sensitive Ink Based on MWCNTs

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# MWCNTs 기반 인쇄형 압력감응잉크의 제조 조건 최적화

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## ABSTRACT

Materials that can be used for 3D printing have been developed in terms of phase and functionality. Materials should also be easily printed with high accuracy. In recent years, the concept of 4D printing has been extended to materials whose physical properties such as shape or volume can change depending on the environment. Typically, such high-performance 3D printing materials include bio-inks and inks for sensors. This study deals with the optimization of the manufacturing method to improve the functional properties of the pressure sensitive material, which can be used as a sensor based on change of the resistance according to the pressure. Specifically, the number of milling for dispersion, the ratio of hardener for controlling elasticity, and the content of MWCNTs were optimized. As a result, a method of manufacturing a highly sensitive pressure-sensitive ink capable of use in 3D printing was introduced.

**Keywords :** Additive Manufacturing(적층제조), 3D Printing(3D 프린팅), Pressure Sensitive Ink(압력감응잉크), MWCNTs(다중벽카본나노튜브), Optimization(최적화)

## 1. Introduction

Additive Manufacturing is a technology that can produce the actual product by an input three-dimensional information of the shape[1]. It is based on Layered manufacturing technology, which implements the three-dimensional shape of the part to be manufactured through the accumulation of planar cross sections[2]. Generally referred to as 3D printing, this technology is a technology in which processes, devices, materials, and software technologies are highly integrated[3]. As described above, it can be considered as a difficult point in technological development that one cannot be developed without

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considering other fields[4]. The recent additive manufacturing technology tends to be developed in utilizing metal materials and highly functional materials[5]. In particular, it also focused on the developments of directly manufacture advanced multi-functional products by a 3D printer by directly manufacture and insert sensors and actuators into the products.

In the manufacture of sensors by 3D printing, some techniques have been developed to measure pressure and to utilize it for tactile sensing application. And various studies are being conducted to integrate these techniques into 3D printing[6-8]. Conventional semiconductor sensors mainly use the piezo phenomenon to measure the force, are commercialized with very accurate and reliable sensors. However, in the manufacturing process of such a semiconductor sensor, in-cooperating 3D printing is not easy. The material of the pressure sensor that can be printed by a 3D printing should satisfy the following three issues. In order to print the first is that it must have sufficient fluidity. This is a feature that it could be accurately accumulated at the printing position through physical or chemical processing. The second is that solidification should be easy after the printing. Curing, cooling, UV light irradiation or chemical treatment can be performed for the solidification. Finally it must have enough sensitivity. In other words, the physical quantity to be measured must have sufficient difference and reliability. These features have been researched in various ways in recent years. Recently, research has been actively conducted on inks of which MWCNTs (Multi-walled carbon nano tubes) are dispersed into elastic PDMS (Polydimethyl siloxane) matrix[9]. The ink can be loaded into a syringe and printed through direct printing technology, and can be easily compounded with a 3D printer[10,11]. This paper introduces methods for producing such printable pressure sensitive inks and the results of research to improve their properties as sensors.


**Fig. 1 Sensor manufacturing system**

# 2. Experiment

## 2.1 Printer

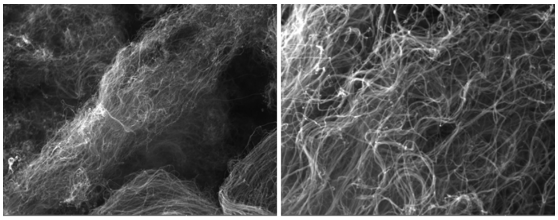
Fig. 1 shows a device for printing pressure sensitive ink using direct write (DW) technology. It is composed of a stage, print heads, and a control unit. The stage of the 3D printer is a gantry type and an auxiliary slider is installed in the x-axis direction. The transfer in the xy plane consists of a linear motor with a large thrust and a linear encoder. Z axis is consisted as AC servomotor. The stage system has a resolution and repeatability of more accurate than ± 1 μm over the full operating range for a sufficient payload of 20 Kg. It consisted of an fused filament fabrication (FFF) type head which produces the outer shape of the sensors and a syringe type dispenser that injects a pressure sensitive ink. The FFF head is a bowden head of the RepRap project. And the syringe-type head is an air pressure dispenser (Accura 8DX, IWASHITA ENGINEERING) in which the ink is put into a general-purpose syringe equipped with a tapered nozzle (TPND-22G, MUSASHI).

The control unit includes a motion controller (LX

504, COMIZOA) for controlling the operation of the stage, a digital input / output ports (SD 404, COMIZOA) for controlling the operation of the head unit, and a control software (3DECON 6.0, NEOHIGHTECH).

## 2.2 Pressure sensitive ink

The pressure sensitive ink is a printable ink which can measure a pressure by the change of electrical resistance with the CNTs dispersed in the elastic nonconductor during deformation. These resistance changes are known to be due to the tunneling effect[12]. The MWCNTs (CNT premium, CARBON NANO TECH) are configured in the form of a cylindrical tube containing a hexagonal carbon ring, and the concentric cylinder contains multiple tubes. In this study the diameter of the CNTs is 10 nm on average, and the ratio of length and diameter is 500 times or more. MWCNTs are a composite structure and has high conductivity and high chemical stability. And these are excellent in tensile strength, and when mixed with thermoplastic or thermosetting compounds, the strength is significantly increased. Although MWCNTs are different depending on the manufacturing method, the product used in this study is shown at Fig. 2.



(a) magnification 29,000 (b) Magnification 110,000

**Fig. 2 Multi walled carbon nano tubes**

**Table 1 Materials for pressure sensitive ink**

| Components | Specification |
|---|---|
| carbon nano-tube | MWCNTs (CNT premium, Carbon nano tech.) |
| polymer | PDMS (Sylgard 184, Dow Corning) |
| solvent | Toluene ($\geq$99.8%, Sigma-Aldrich) |
| surfactant | Sodium dodecyl sulfate (SDS,$\geq$99.0%, Sigma-Aldrich) |

The material used for the elastic nonconductor is PDMS, which is consist of main material (Sylgard 184-A, DOW CORNING) and curing agent (Sylgard 184-B). Flexibility and elasticity can be adjusted depending on the content of curing agent. In this experiment, PDMS was cured through heating, but it also cured at room temperature with in 48 hours.

The ink manufacturing process is done with the dispersion 0.1, 0.15, 0.2 g of MWCNTs with 20 g toluene (Toluene, 99.8%, Sigma-Aldrich) solvent and

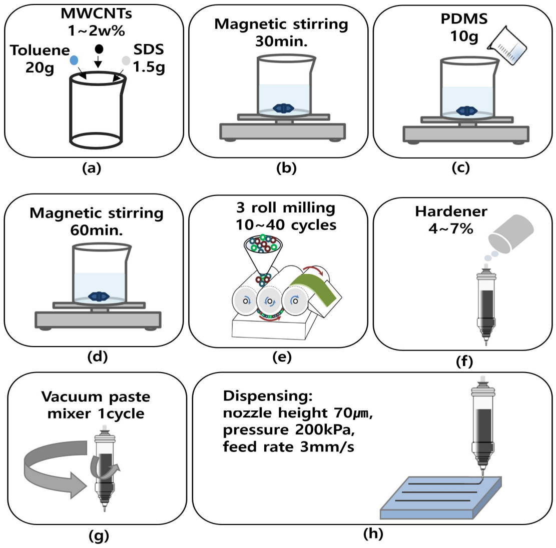
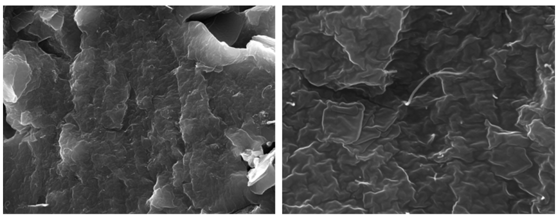



**Fig. 3 Ink fabrication process**



(a) magnification 10,000 (b) Magnification 50,000

**Fig. 4 photography of the MWCNTs in PDMS**

1.5 g of SDS (sodium dodecyl sulfate, 99.0%, Sigma-Aldrich) surfactant in a 100 ml beaker. By a magnetic stirrer (GLHPS-C12, GLOBAL LAB) the solution is mixed for 30 minutes so that MWCNTs and SDS mixed well. After 10g of PDMS main material was added to the mixture, it stirred for an hour. Then it subjected to three roll milling (EXAKT 80E, Germany). Three-Roll miller is consisted of three rolls and is an effective equipment that can disperse and mix a high viscous materials. And the degree of dispersion changes according to the gap of the rolls and the number of cycles repeated. Therefore, in this experiment, the interval of Roll was fixed at minimum gap with medium rolling speed. With this roll milling the ink is finally prepared before use except adding hardener which mixed just before dispensing. The material used to make the pressure sensitive material is shown in Table 1. After injecting the pressure sensitive ink into the dispensing syringe together with an appropriate amount of curing agent, a vacuum paste mixer (SK-300V, KAKUHUNTER) was used to mix hardener and eliminate voids. Fig. 3 shows the manufacturing process of the pressure sensitive ink described above. Fig. 4 is a photograph taken by FE-SEM after curing the pressure sensitive ink produced by loading 1.5 wt% of MWCNTs. Fig. 4(a) shows a cross section surface by torn out, and the point or curve in white color in Fig. 4(b) is the MWCNTs.

## 2.3 Sensor fabrication

The process of manufacturing the test sensor to optimize the pressure sensor characteristics is shown in Fig. 5. According to the procedure, it can be divided into the following five steps. As a first step, pins are soldered at 2.6 mm intervals on the PCB substrate, and this serves as a terminal for reading an electrical signal from the sensors. Second, using the direct write technology, the pressure sensitive material mixed with the curing agent is dispensed between the pins, which will be a sensor. Third, the dispensed

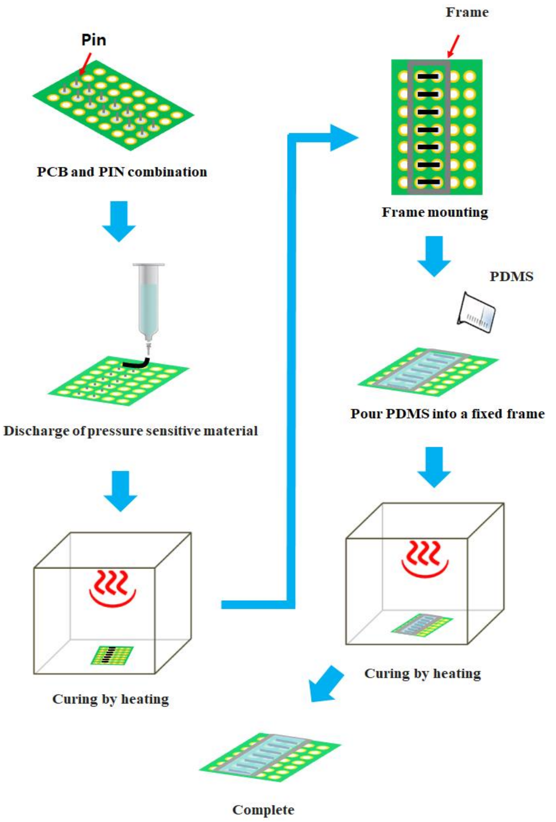



**Fig. 5 Test part fabrication**

pressure sensitive ink is thermally cured at 80°C for 2 hours using a thermal chamber. Fourth, pour and coat PDMS on the sensor to prevent damage to the sensor during measuring test. The PDMS used in the sensor coating is also elastic after curing at a mass ratio of 10:0.6 of the main to the curing agent. The final step is to cure for another 2 hours at 80°C. Of course, curing of PDMS using the third and fifth steps may eliminated when a curing during 48 hours at ambient temperature is preferred.

# 3. Optimization

The sensor developed in this research was manufactured for the main purpose of being utilized in the tactile sensor of a robots while being able to be manufactured by 3D printing. Therefore, sensitivity

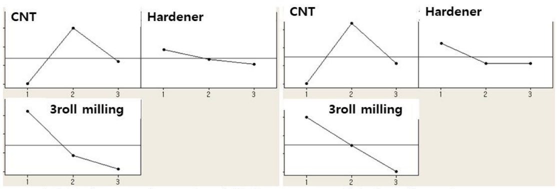
**Table 2 Test conditions and measurement results**

| 3 Roll mill cycles | | | 10(1) | | | 25(2) | | | 40(3) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Hardener(wt%) | | | 4(1) | 5.5(2) | 7(3) | 4(1) | 5.5(2) | 7(3) | 4(1) | 5.5(2) | 7(3) |
| MWCNTs (wt%) | 1.0 (1) | resistance(kΩ) | 6100 | 5400 | 5700 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | | △T(sec) | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | | △V(V) | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | 1.5 (2) | resistance(kΩ) | 70 | 216 | 341 | 377 | 900 | 1000 | 1000 | 1200 | 1700 |
| | | △T(sec) | 0.7 | 2 | 1 | 2 | 2 | 2 | 2 | 2 | 2 |
| | | △V(V) | 0.9 | 0.6 | 0.55 | 0.5 | 0.03 | 1.2 | 0.0v | 0.1 | 0.07 |
| | 2 (3) | resistance(kΩ) | 195 | 27 | 138 | N.A. | 1200 | 1700 | 5000 | 7000 | 32000 |
| | | △T(sec) | 2 | 1 | 2 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | | △V(V) | 0.1 | 0.24 | 0.18 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |

and response speeds are considered to be the most important sensor characteristics. At this time, the sensitivity was measured by the amount of change in the output voltage value caused by the change in resistance of the sensor with respect to a constant compressive force of 10N. Also, the response speed was measured at a time when the sensor was resiliently restored and reliable restored within about 2% of the initial output voltage when the compressive force applied in the above sensitivity experiments was removed. The main variables of the ink manufacturing process were optimized to improve sensitivity and response speed.

### 3.1 Parameters

At this time, the most affecting factors on the two sensor properties are selected based on basic experiments, and is the ratio of the curing agent, the number of roll milling times and the content of MWCNTs. The proportion of curing agent is chosen as it is believed to be a major factor determining the




(a) Voltage drop (at 10N)  (b) Settling time

**Fig. 6 Test results by the parameter levels**

elasticity of the sensor and to have a significant effect on the response speed. Since the number of 3 roll millings has a great influence on the degree of dispersion of MWCNTs, it was judged and selected to have a significant influence on the content of MWCNTs and the conductivity of the sensor.

Table 2 shows the experimental factors and its experimental results. The three levels of content of MWCNTs were 1.0 wt%, 1.5 wt%, 2 wt% and curing agent of 4%, 5.5%, 7% were chosen for the testing percentage. Also, the number of cycles of three roll milling was selected as 10, 25 and 40 Cycles. Toluene 20 g, PDMS 10 g and SDS 1.5 g is in fixed usage. In the experiment, sensors were manufactured under 27 different conditions, and the resistance with no pressure, the voltage changes at a specified pressure, and the time to stabilize at restoration were measured. "N.A." was recorded if the resistance without pressure was too high and the measuring instrument cannot give the readouts or too low below 0.1V. When the response speed was 2 seconds or more, it was recorded as "2 sec". This is because for a tactile sensor it should have bigger change in output voltage of 0.5V and a response speed of less than 1 second is required.

The results of analyzing the effects of the above experiment are shown in Fig. 6. The results of voltage and time represents the combination of optimum levels with MWCNTs 1.5%, Cycle 10 times, hardener 4 wt% is optimal in these cases.

### 3.2 Application case

Fig. 7 shows the used test device for measuring the output characteristic of the produced sensor. Attached a digital push & pull gauge (SH-20, SUN DOO INSTRUMENTS) to the Z stage (ENKIT 1000, WIKAN) for testing, by control the position and speed it applied 10N of load. The output voltage of the sensor measured through the DAQ device. And was recorded as a graph of the output voltage against time through the TMea program created in LabVIEW (NATIONAL INSTRUMENTS). Fig. 8 shows the active response of the sensor when it pushed with 10N. And is manufactured by the optimum pressure sensitive ink. At this time, it can be seen that the change in output voltage is 0.9V, and the settling time on pressure removal is less than 1 second.

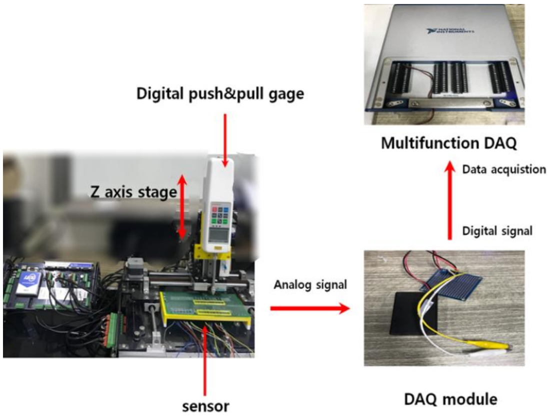



**Fig. 7 Device of sensor measurement**

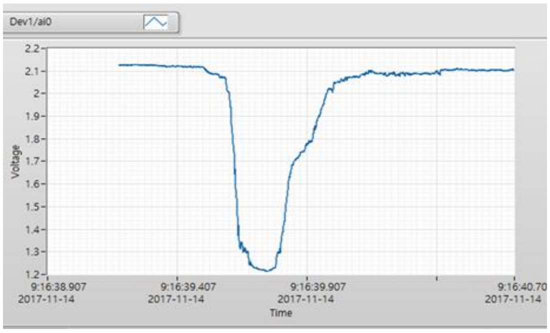



**Fig. 8 Graph of output voltage versus time**

## 4. conclusions

In this paper, a pressure sensitive ink fabrication method is optimized for robotic application. And it is suitable to additively manufactured by using the direct write technology. The main material used was MWCNTs, which were dispersed in the elastic insulator PDMS. The sensor fabrication conditions were derived by conducting 27 different fabrication experiments. And a pressure sensor is manufactured according to the conditions and show it could be used as a tactile sensor printing applications.

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