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REGULAR PAPER

Development of a TPU/CNT/Cu Composite Conductive Filament with a High CNT Concentration

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Abstract

In this study, a flexible conductive filament was fabricated by mixing thermoplastic polyurethane (TPU), carbon nanotubes (CNTs), and Cu powder. A polymer extruder was used to disperse conductive materials in the TPU matrix. Because the dispersion of CNTs in polymers is difficult, the dispersion process was repeated several times for the homogeneity of the fabricated conductive filament. Cu powder with high electrical conductivity was additionally added to improve the electrical characteristics of the conductive polymer. As TPU generally has excellent ductility and durability, the fabricated filament can secure flexibility. The resistance was measured and compared according to the mixing ratio of CNT/Cu powder. Based on the obtained results, the resistance of the conductive filament decreased as the CNT and Cu powder contents were increased. The addition of metal powders, such as CNTs and Cu powder, however, reduced the ductility of TPU. Finally, the developed conductive filament was used to fabricate a simple closed photodiode circuit.

Keywords Conductive filament · TPU/CNT composite · 3D printing · Flexible composite

1 Introduction

Conductive composite materials are used in various areas, such as flexible circuits, flexible displays, wearables, and sensors, as they are highly suitable for the mechanical and electrical characteristics of flexible devices [1]–[5]. In addition, liquid or solid conductive composite materials are actively used in areas where printing technology is required because pneumatic injection or additive manufacturing technology can be easily applied to them. However, because they are printed on flexible electronic devices with an irregular and curved plane, flexibility and durability, including bending, folding, and twisting are required in addition to electrical conductivity stability [6].

Among various conductive composites, conductive polymer composites facilitate direct 3D printing, as they do not require solvents, complex processes, and additional processes, such as thermal annealing, which are required for manufacturing metal ions, ink, and paste. In addition, they have longer lifespan than the described conductive materials and can be produced in the form of a filament [7]. Conductive polymer composites have high commercial potential owing to high moldability and low density, electrical characteristics by conductive materials, and excellent flexibility and durability of the polymer matrix [8]. Therefore, the production cost of the conductive polymers and their applicability to printing have been examined [6, 9].

Carbon nanotubes (CNTs) are difficult to disperse in the polymer structure owing to their high cohesive properties. Further, high energy is required, as their concentration increases owing to an increase in the viscosity of the molten composite [10]. However, they have high electrical conductivity because of the low percolation threshold and high aspect ratio [11]. CNTs are also commonly used as composite materials owing to their excellent mechanical and thermal properties. In particular, conductive composites can be produced by forming a conductive path in insulating polymers with low density and high moldability, such as thermoplastic polyurethane (TPU) and PETG, by adding CNTs. As conductive polymers are easy to manufacture and have high printability, various conductive materials, such as CNTs [12], carbon black [13], carbon nanofiber [14],

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graphite [12], and graphene [15], have been mixed with the polymer structure in many studies.

With rapidly increasing interest in 3D additive manufacturing technology, Cu powder as a conductive material, was mixed with ABS, PLA, and PS, which are most commonly used as commercial filaments [16, 17]. It was reported that highly conductive filaments could be manufactured, and high percolation threshold values were observed when Cu powder was added. The polymers of commercial filaments, however, have high hardness and insufficient durability for bending.

No case has been reported for TPU/CNT and TPU/CNT/Cu composite conductive filaments with high CNT concentration (12% or higher). Therefore, in this study, a TPU/CNT composite filament was fabricated by including high-concentration CNTs in the TPU matrix, and the resistance was measured and analyzed while flexibility was maintained. In addition, Cu powder was added and its effect on the resistance of the TPU/CNT composite was observed. The dispersion process was repeated to obtain homogeneous electrical characteristics of the conductive composite.

2 Experiment

2.1 Materials

Table 1 shows the properties of the materials used in this study. Huada Electronic Design Co., Ltd HD-E290I9 TPU was used to secure flexibility and durability, and Kumho Petrochemical Co., Ltd. (KKPC) K-Nanos 210P MWCNT was added as a conductive material to be dispersed in the TPU matrix. AV-CU003045US 45 µm/spherical Cu powder from AVENTION Co., Ltd. was added to secure additional electrical performance.

2.2 Manufacturing and Mixing Process

Homogeneous dispersion of CNTs in polymer matrix structures is difficult owing to their strong agglomeration properties caused by high surface energy. Polymer extruders are commonly used, as they facilitate the dispersion of the filler in the polymer structure as a melting mixing method that uses thermal and shear force. Therefore, in this study, the melting mixing method was used during the manufacturing of the conductive filament for the homogeneous dispersion of CNTs in TPU.

Table 1 Material properties

	TPU	CNT	Cu
Melting point [℃]	200	3550	1084
Density [g/cm^3]	1.19	0.025	8.96
Particle size [µm]	3.6×10^3	0.01	45

Figure 1 shows the conductive filament manufacturing process. When the materials to be mixed are placed in the hopper in sequence, they are transported to the nozzle section by the shear force of the screw inside the cylinder. Meanwhile, TPU is melted by the heat source of the coil heater. The materials are then gradually stagnated in the nozzle section, thereby forming a pressure inside the nozzle space. The formed pressure, which is generated by the molten TPU with relatively high viscosity, causes mixing with conductive materials. The nozzle is filled with the mixed materials, and the internal shear force generates a pressure in the nozzle section direction, thereby extruding the mixture through the nozzle with a diameter of 1.5 mm. The temperature of the coil heater was set to 250 ℃ and the screw speed was 15 RPM.

When the degree of CNT dispersion is low, the electrical characteristics of the extruded conductive filament are not uniform. Therefore, the dispersion process was repeated by shearing the fabricated conductive filament wire into small sizes as shown in Fig. 2

2.3 Resistance and homogeneity measurement

The entire length of the extruded filament sample was cut into three pieces (start, middle, and end pieces), as shown in Fig. 3, and the standard deviation of the measured resistance was calculated to confirm homogeneity $\left(R_E \cong R_M \cong R_S\right)$ of fabricated conductive filament. The resistance was measured using a multimeter, and the measured values were averaged. The measured resistance was converted into the volume

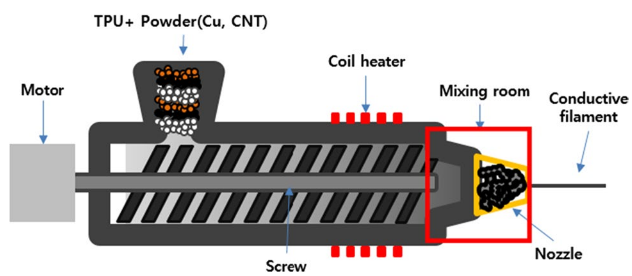

Fig. 1 Melt mixing method for conductive filament manufacture process

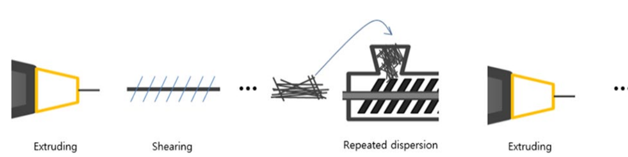

Fig. 2 Repeating the dispersion process

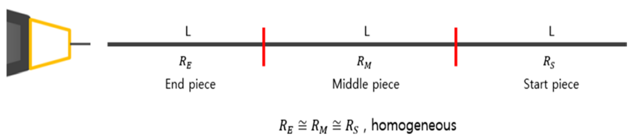

Fig. 3 Resistance measurement section and the homogeneity of conductive filament

Fig. 4 Four times dispersion of TPU/CNT 15 wt%

resistivity, $\rho(\Omega$ cm), using Eq. (1) for analysis. In Eq. (1), A $\left(mm^2\right)$ is the cross-sectional area, and L (mm) is the filament length.

$$\rho = R \cdot A/L \quad (1)$$

3 Result and discussion

3.1 High weight fraction CNT wt% TPU/CNT composite

Figure 4 shows the results of repeating the dispersion process of CNT 15% four times. After repeating the dispersion process four times, the stiffness of the filament was maintained, and excellent surface roughness could be observed. As the CNT content increases, higher energy is required for dispersion because of an increase in the viscosity of the molten composite. Therefore, the results described above are considered to originate from the increasing CNT percolation capability in the TPU matrix due to repeated heating–shearing processes. In all TPU/CNT filament cases, dispersion was performed four times. Excellent flexibility and durability were observed under the application of twisting and bending for up to CNT 23%, but the fabrication failed from 25% owing to the high viscosity caused by poor surface roughness (Fig. 5).

Figure 6 shows the standard deviation of the resistance of the fabricated filament calculated to examine homogeneity due to dispersion. As the percentage of CNT increased, the standard deviation decreased, showing that the distribution of CNT phases in TPU became easier. In other words, at a high CNT concentration, sufficient homogeneity can be secured even under low dispersion. In addition, high CNT concentration is considered to be favorable in terms of quality.

Fig. 5 Four times dispersion of TPU/CNT filament with high CNT wt%: 23.3% (left), 25% (right)

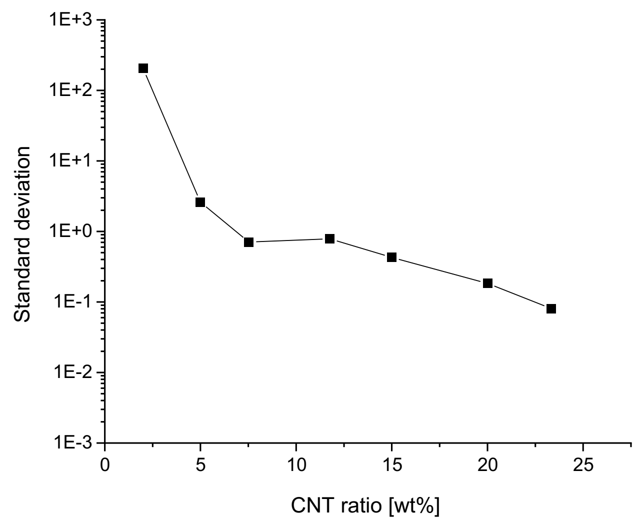

Fig. 6 Measured volume resistivity standard deviation on CNT ratio [wt%] in a TPU/CNT composite

Table 2 Reported percolation threshold in the literature

	Percolation threshold CNT, wt%	Resistivity Ω cm
Bertollini et al. [18]	2	1.0×10^2
Sui et al. [10]	3	1.0×10^3
Ramoa et al. [19]	3	4.3×10^1
Kim et al. [20]	4	1.43×10^1
N.P. Kim [8]	8	7.0×10^5

CNT has a low percolation threshold because its high aspect ratio makes it possible to obtain high electrical conductivity with only a small amount of the filler. Table 2 summarizes the reported percolation thresholds of TPU/CNT composites. It can be seen that each percolation threshold is different. This appears to be due to the low degree of CNT dispersion in polymer and the difference in temperature, RPM, and measuring equipment during dispersion. Compared to the relatively high volume resistivity of TPU (1.0×10^{12} Ω cm), the percolation threshold was found to be CNT 5% (1.38×10^{1} Ω cm) in this study. The obtained result is similar to that by Kim et al. (CNT 4%, 1.43×10^{1} Ω cm).

Figure 7 shows the volume resistivity according to the percentage of CNT. As the percentage of CNT is increased, the volume resistivity decreased. The lowest volume resistivity of 0.12 Ω cm is obtained at CNT 23%, which is the maximum content applicable. The results obtained under the conditions of 240 ˚C/6 RPM/3 times and CNT 12% (1.44×10^{2} Ω cm) by N.P. Kim were compared with those under the conditions of 250 ˚C/15 RPM/4 times and CNT 11.7% (2.27 Ω cm) in this study. From this comparison, the results of this study were found to be superior. High-concentration CNTs easily agglomerate even with a slight temperature change owing to the increased viscosity. Thus, higher energy is required for dispersion. Under the same dispersion method, it was difficult to identify a clear correlation with temperature for high percentage of CNT, but RPM was considered to be dominant. To explore this, the influence of the temperature and shear force (RPM) on dispersion and resistance according to the percentage of CNT should be examined in the future. In the results of Sui et al. and Ramoa et al., high dispersion was induced by applying thermal and shear forces over an extended period of time. This procedure has the same principle as repeated dispersion performed in this study.

3.2 TPU/CNT/Cu composite

Figure 8 shows the reduction in CNT mass in the total ratio. TPU and Cu mass were kept constant, and as the percentage of CNT decreased, the ratio of the percentage of Cu in the total ratio increased. When Cu ratio was increased under the same the percentage of CNT, the resistance reduction effect was observed (Table 3). This is because Cu powder can easily form a conductive path by facilitating the electron movement. As shown in Fig. 8, however, the volume resistivity increases with the percentage of Cu. This appears to be due to the reduction in the percentage of CNT rather than the increase in the Cu powder concentration. Podsiadly et al. reported that the percolation threshold was observed at polymer/Cu 80% [17]. We can conclude that for TPU/CNT/Cu in this study, the electrical resistance depends on the percentage of CNT because the percentage of Cu is relatively low.

Figure 9 shows the volume resistivity according to the Cu content at high percentage of CNT. It can be seen that the resistivity decreases by approximately 1.3 times at Cu 23%, as compared to Cu 9%. At a relatively higher percentage of CNT, the addition of Cu powder has no significant impact on the resistance. Moreover, the hardness increases, and the flexibility significantly decreases. When CNT 19.2%/Cu 23% were exceeded, high hardness was observed due to brittleness, and flexibility could be not secured owing to easy fracture during bending.

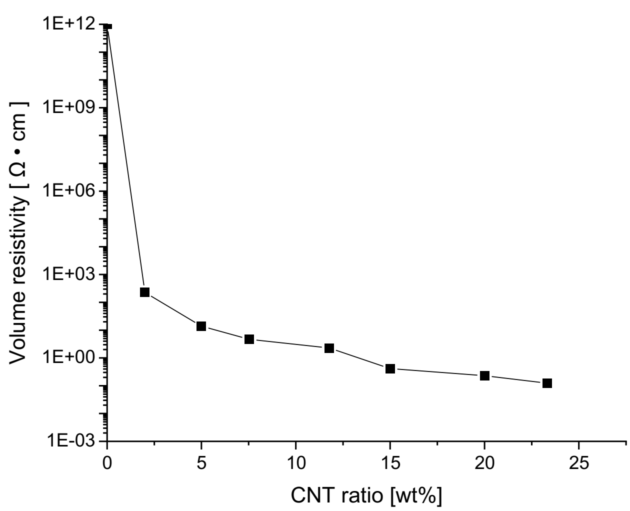

Fig. 7 Measured volume resistivity versus CNT ratio [wt%] in a TPU/CNT composite

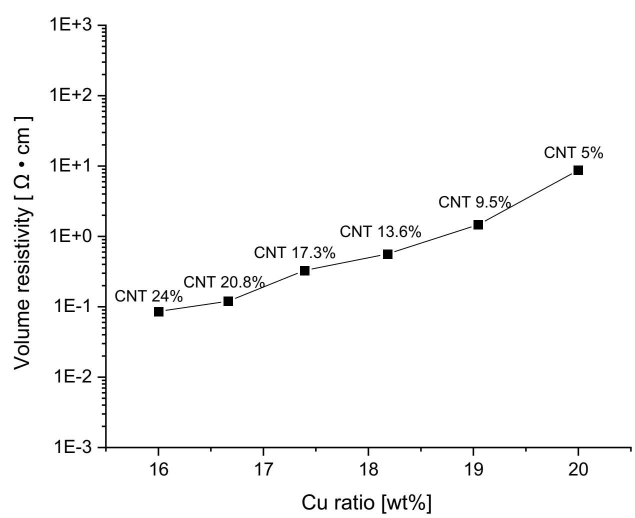

Fig. 8 Measured volume resistivity versus Cu ratio [wt%] in a TPU/CNT/Cu composite

Table 3 TPU/CNT and TPU/CNT/Cu comparison

Composition (Remaining TPU)	Resistivity (Ω cm)
CNT 5%	13.84
CNT 5%/Cu 20%	8.72
CNT 20%	0.23
CNT 20%/Cu 16.6%	0.12

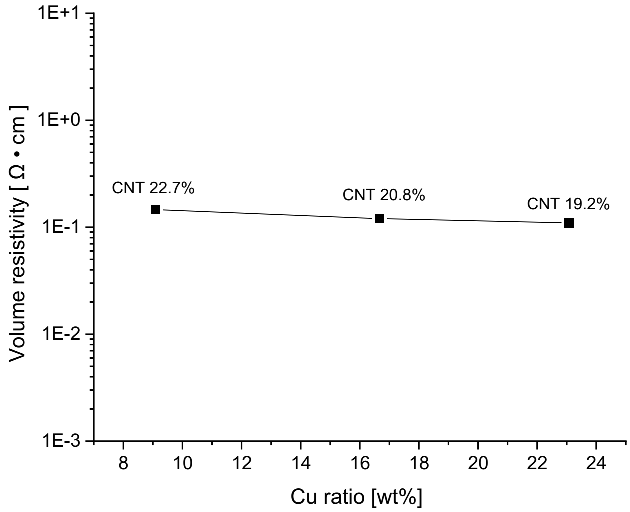

Fig. 9 Measured volume resistivity versus Cu ratio [wt%] in TPU/CNT/Cu with high concentration CNT

4 Conclusion

In this study, TPU/CNT composite was fabricated by including high CNT concentration in TPU. In addition, Cu powder was added to the TPU/CNT composite to analyze its effect on the resistance. As melt mixing method, the thermal and shear force was used to disperse conductive materials in the TPU matrix.

CNT dispersion in the polymer structure is difficult owing to the high surface energy. Thus, dispersion needs to be repeated several times to secure homogeneous electrical characteristics of the fabricated conductive composite filament. The standard deviation of the conductive composite resistance was low after repeating the dispersion procedure four times, and excellent flexibility and filament stiffness were maintained simultaneously.

As the percentage of CNT was increased, the volume resistivity decreased. The percolation threshold was found to be 5%, and excellent flexibility and durability were observed for up to 23%. The volume resistivity was found to be 0.12 Ω cm for the TPU/CNT 23% composite and 0.11 Ω cm for the TPU/CNT 19.2%/Cu 23% composite. The addition of CNTs and Cu powder, which are conductive materials, could reduce the electrical resistance by facilitating the electron movement. At the same the percentage of CNT, the addition of Cu powder decreased the volume resistivity. At a high CNT concentration, however, the addition of Cu did not improve the volume resistance significantly. Moreover, the addition of CNTs and Cu powder in large quantities to TPU reduced ductility and led to easy fracture due to brittleness.

A simple closed photodiode circuit was manufactured using the fabricated conductive composite filament (Fig. 10). The conductive composite filament developed in this study

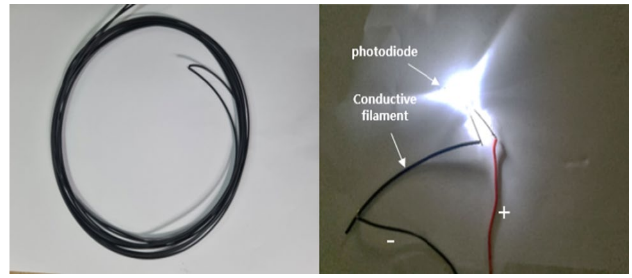

Fig. 10 Conductive composite filament (left) and closed circuit(right)

can be applied to circuits and sensors in various fields. In the future, printing characteristics will be investigated using 3D printing, and changes in resistance due to the tension and bending of the output will be researched.

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Authors' contributions All authors contributed to this paper. Experiments were performed by Hansol Kim, Seungcheol Shin, Hojin You. Data analysis and result considerations were performed by Hansol Kim, Sang-Woo Han, Inhwan Lee and Jungho Cho. The first draft of the manuscript was written by Hansol Kim and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

References

1. Lee, S., et al. (2015). Ag nanowire reinforced highly stretchable conductive fibers for wearable electronics. *Advanced Functional Materials, 25*(21), 3114–3121.
2. White, M. S., et al. (2013). Ultrathin, highly flexible and stretchable PLEDs. *Nature Photonics, 7*(10), 811–816.
3. Matsuhisa, N., et al. (2015). Printable elastic conductors with a high conductivity for electronic textile applications. *Nature Communications, 6*(May), 1–11.
4. Xu, F., & Zhu, Y. (2012). Highly conductive and stretchable silver nanowire conductors. *Advanced Materials, 24*(37), 5117–5122.
5. Park, M., Park, J., & Jeong, U. (2014). Design of conductive composite elastomers for stretchable electronics. *Nano Today, 9*(2), 244–260.
6. Hu, Y., et al. (2016). Low cost and highly conductive elastic composites for flexible and printable electronics. *Journal of Materials Chemistry C, 4*(24), 5839–5848.
7. Kwok, S. W., et al. (2017). Electrically conductive filament for 3D-printed circuits and sensors. *Applied Materials Today, 9*, 167–175.
8. Kim, N. P. (2020). 3D-printed conductive carbon-infused thermoplastic polyurethane. *Polymers (Basel)., 12*(6), 205.
9. Leigh, S. J., Bradley, R. J., Purssell, C. P., Billson, D. R., & Hutchins, D. A. (2012). A simple, low-cost conductive composite material for 3D printing of electronic sensors. *PLoS ONE, 7*(11), 1–6.
10. Sui, G., Liu, D., Liu, Y., Ji, W., Zhang, Q., & Fu, Q. (2019). The dispersion of CNT in TPU matrix with different preparation methods: Solution mixing vs melt mixing. *Polymer (Guildf)., 182*, 121838.

11. Shehzad, K., et al. (2013). Effects of carbon nanotubes aspect ratio on the qualitative and quantitative aspects of frequency response of electrical conductivity and dielectric permittivity in the carbon nanotube/polymer composites. *Carbon New York, 54*, 105–112.
12. Gnanasekaran, K., et al. (2017). 3D printing of CNT- and graphene-based conductive polymer nanocomposites by fused deposition modeling. *Applied Materials Today, 9*, 21–28.
13. Zhang, J., Yang, B., Fu, F., You, F., Dong, X., & Dai, M. (2017). Resistivity and its anisotropy characterization of 3D-printed acrylonitrile butadiene styrene copolymer (ABS)/carbon black (CB) composites. *Applied Science, 7*(1), 1150.
14. Rymansaib, Z., et al. (2016). All-polystyrene 3D-printed electrochemical device with embedded carbon nanofiber-graphite-polystyrene composite conductor. *Electroanalysis, 28*(7), 1517–1523.
15. Palenzuela, C. L. M., Novotný, F., Krupička, P., Sofer, Z., & Pumera, M. (2018). 3D-printed graphene/polylactic acid electrodes promise high sensitivity in electroanalysis. *Analytical Chemistry, 90*(9), 5753–5757.
16. Experimental, M. P. C. (2022). *Conductivity Behaviour under Pressure of Copper and Modelling*. Springer.
17. Podsiadły, B., Skalski, A., Wałpuski, B., & Słoma, M. (2019). Heterophase materials for fused filament fabrication of structural electronics. *Journal of Materials Science: Materials in Electronics, 30*(2), 1236–1245.
18. Bertolini, M. C., Ramoa, S. D. A. S., Merlini, C., Barra, G. M. O., Soares, B. G., & Pegoretti, A. (2020). Hybrid composites based on thermoplastic polyurethane with a mixture of carbon nanotubes and carbon black modified with polypyrrole for electromagnetic shielding. *Frontiers in Materials, 7*(June), 1–9.
19. Ramôa, S. D., Barra, G. M., Oliveira, R. V., De Oliveira, M. G., Cossa, M., & Soares, B. G. (2013). Electrical, rheological and electromagnetic interference shielding properties of thermoplastic polyurethane/carbon nanotube composites. *Polymer International, 62*(10), 1477–1484.
20. Kim, K., Park, J., Suh, J. H., Kim, M., Jeong, Y., & Park, I. (2017). 3D printing of multiaxial force sensors using carbon nanotube (CNT)/thermoplastic polyurethane (TPU) filaments. *Sensors and Actuators A Physical, 263*, 493–500.

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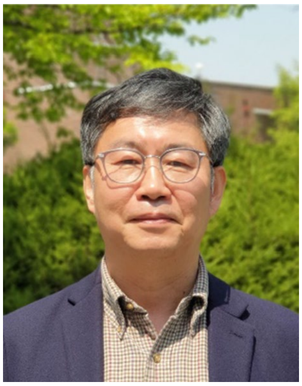

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