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Flexible tactile sensor materials based on carbon microcoil/silicone-rubber porous composites

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ABSTRACT

Mechanical and electrical properties of porous composites consisting of spring-shape carbon microcoils (CMCs) and silicone-rubber were investigated. The CMC/rubber porous composites having 71–81% porosity had compressive elastic moduli of 0.04–0.1 MPa which were 2–4% of a composite having the same ingredients without pores. The porous structure gave the composites not only the flexibility but a unique piezoresistivity in a wide compressive strain range. Resistivities of the porous composites increased over 10^4 times with a compressive strain up to 80%, while those of other porous composites including fibrous or particulate carbon fillers decreased only several tens of percent. CMC/rubber porous composites having such a unique piezoresistivity enabled us to develop a new tactile sensor system.

1. Introduction

Robotics technology has attracted much attention in the fields of nursing care and life support in recent years. Robots used in the fields must be equipped with several devices for ensuring human safety. In particular, a tactile sensor is one of the important safety devices because the sensor is installed on contact points between robots and humans. The tactile sensor is expected to have enough flexibility and softness to protect delicate human bodies [1–4].

We and other groups chose a combination of a flexible polymer as a base material and a carbon filler as a conductive material to produce flexible tactile sensor materials [5–8]. The resulting carbon filler/polymer composites have a piezoresistive property; when compressive stress is applied on the carbon filler/polymer composite, included carbon fillers approach with one another to form conducting paths, leading to decreases in resistivity of the composite. We recently reported remarkably flexible composites consisting of Ketjenblacks and silicone-rubber [8]. Their flexibility was based not only on silicone-rubber but also on continuous pores in the composites. Introduction of the pores afforded a piezoresistive property in a wide compressive strain range of 0–80% to the composites.

Carbon fillers are also an important factor determining mechanical and electrical properties of the composites, and solid carbon fillers, such as carbon blacks, carbon nanotubes, and carbon nanofibers, have often been researched as conductive materials [9–12]. A flexible carbon filler of CMCs has also attracted much attention because of the unique conformation and properties; a CMC having spring-shape of 1–10 μm in coil diameter can deform under a slight load [13–15]. Even when included in a flexible matrix, the CMC extended and/or bent together with the matrix under applying load [13]. This flexibility of CMCs prompts us to add the filler into a flexible matrix of porous silicone-rubber. In this study, we revealed mechanical and electrical properties of CMC/rubber porous composites compared with the porous composites including fibrous vapor grown carbon fibers (VGCFs) or particulate Ketjenblacks (KBs).

2. Material and methods

2.1. Materials

Silicone-rubber (Shin-Etsu Chemical Co., Ltd., KE-118) was used as a matrix. The density and resistivity were about 1.14 g/cm^3 and 4×10^{14} Ω cm, respectively.

CMCs with the length of 45–90 μm, 90–150 μm, and 150–300 μm were prepared by a conventional method [16]. The average fiber and coil diameters of CMCs were 0.7 μm and 5 μm,

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respectively. VGCFs (Showa Denko K. K., VGCF) and KBs (Lion Corporation, ECP600JD) were also used as fillers. The diameter and length of VGCFs were 0.15 μm and 10–20 μm, respectively. The average diameter of KBs was 34 nm. Resistivities of CMCs, VGCFs and KBs were about 10^{-2}, 10^{-4}, and 10^{-1} Ω cm, respectively. In addition, densities of CMCs, VGCFs and KBs were 1.9, 2.0, and 2.0 g/cm^3, respectively.

NaCl particles with average diameters of ca. 50 μm (Tomita Pharmaceutical Co., Ltd., 250 M), ca. 120 μm (Nihonkaisui Co., Ltd., EF-100), ca. 320 μm (Nihonkaisui Co., Ltd., EF-300), and ca. 490 μm (Wako Pure Chemical Industries, Ltd., 198–01675) were used as a material for making porous structures. The average diameters were calculated from optical microscope images of their particles. The NaCl particles were used after dried at 110 °C for 2 h.

2.2. Fabrication of test pieces

Composites were prepared from silicone-rubber prepolymer, carbon fillers, and NaCl particles, as shown in Table 1. Hexane was used as a solvent as needed to decrease viscosity of the mixture. After they were mixed by hand for 5 min and degassed in a vacuum for 1 min, the mixture was cured at a room temperature for 4 days. The obtained composites were cut into 10 mm × 10 mm × 10 mm blocks (Type I) and 15 mm × 80 mm × 6 mm blocks (Type II). Then they were washed with water for several times to remove NaCl particles. The obtained porous composites were dried completely in a dryer at 110 °C for 2 h. Three test pieces were made for each composite.

2.3. Observation and analysis of porous structures

Porous structures of the composites were observed by SEM (FEI Company, Quanta 200). Bulk densities of the composites were calculated from the outside dimensions and weights. The true densities were measured by using Micromeritics Gas Pycnometer (Shimadzu Corporation, Accupyc1330). The values of porosity Φ were calculated from the bulk density ρ_b and true density ρ_t as follows.

$$\Phi = 1 - \rho_b/\rho_t \quad (1)$$

2.4. Compressive test and resistivity measurement

A compressive test was carried out for Type I test pieces using a universal testing machine (Instron Japan Co., Ltd., 5582) at a constant strain speed of 10%/min. Compressive elastic moduli of the test pieces were calculated from the crosshead displacements and applied loads.

Resistances of the Type I test pieces were measured using a multimeter (Iwatsu Test Instruments Corporation, VOAC7523) with a range of 10^{-4} Ω–5×10^8 Ω, as shown Fig. 1a and b (Type I-1 and Type I-2). Compressive strain was applied at 100%/min. The measured values were converted into resistivities based on dimension values of the composites. Resistances of Type II test pieces were also measured in two ways; electrodes with the length of 15 and 80 mm were set at intervals of 60 and 5 mm in Type II-1 and Type II-2, respectively (Fig. 1c and d). Compressive strain was applied at 100%/min in the area of 5 mm × 5 mm, 10 mm × 10 mm, and 15 mm × 15 mm using a glass plate for each test piece. These experiments were carried out three times.

3. Results

3.1. Observation and analysis of porous structures

Fig. 2 shows the SEM images of CMC/rubber porous composites prepared from NaCl particles with average diameters of 50, 120,

Table 1
Ingredients of investigated composites.

Sample	Filler	Filler content (wt%)	Diameter of NaCl particles[a] (μm)
M-320	–	–	320
45C5-320	CMC (45–90 μm)	5	320
45C8-320	CMC (45–90 μm)	8	320
45C10-320	CMC (45–90 μm)	10	320
45C12-320	CMC (45–90 μm)	12	320
45C14-320	CMC (45–90 μm)	14	320
45C16-320	CMC (45–90 μm)	16	320
90C1-320	CMC (90–150 μm)	1	320
90C3-320	CMC (90–150 μm)	3	320
90C5-320	CMC (90–150 μm)	5	320
90C7-320	CMC (90–150 μm)	7	320
90C9	CMC (90–150 μm)	9	–
90C9-50	CMC (90–150 μm)	9	50
90C9-120	CMC (90–150 μm)	9	120
90C9-320	CMC (90–150 μm)	9	320
90C9-490	CMC (90–150 μm)	9	490
90C11-320	CMC (90–150 μm)	11	320
150C3-320	CMC (150–300 μm)	3	320
150C4-320	CMC (150–300 μm)	4	320
150C5-320	CMC (150–300 μm)	5	320
150C6-320	CMC (150–300 μm)	6	320
V1-320	VGCF	1	320
V3-320	VGCF	3	320
V5-320	VGCF	5	320
V7-320	VGCF	7	320
K1-320	KB	1	320
K2-320	KB	2	320
K3-320	KB	3	320
K5-320	KB	5	320

[a] Weight ratios of NaCl particles were 4 times of the prepolymer.