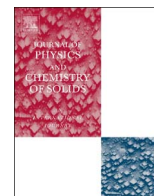




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## Contact resistance of multi-walled carbon nanotube/natural rubber nanocomposites with metallic ball

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## ABSTRACT

This paper reports on the contact resistance ( $R_c$ ) between carbon filler/natural rubber (NR) nanocomposite and gold ball: three varieties of nanocomposites were prepared from carbon black (CB) and two kinds of multi-walled carbon nanotubes (MWCNTs) with different diameter.  $R_c$  of MWCNT/NR nanocomposite was remarkably less than that of CB/NR nanocomposites. The relationship between  $R_c$  of MWCNT/NR nanocomposites and applied load was expressed in the formula,  $R_c = C \cdot P^{-n}$  ( $P$ : load,  $C$  and  $n$ : constant): for the MWCNTs (diameters of 13 nm)/NR and MWCNTs (diameters of 67 nm)/ NR nanocomposites, they were expressed as  $R_c = 1724 \cdot P^{-0.6}$  and  $R_c = 344 \cdot P^{-0.37}$ , respectively. The former (MWCNT,  $\phi$ 13 nm) showed higher  $R_c$  than the latter (MWCNT,  $\phi$ 67 nm) over whole region of applied load. The mechanical hardness of the former was higher (90 HsA) than that of the latter (82 HsA). Therefore, the smaller contact area between the nanocomposite and gold ball of the former resulted in higher  $R_c$ . The apparent specific contact resistivity was calculated from the observed values of  $R_c$  and contact area:  $130 \Omega \text{ mm}^2$  and  $127 \Omega \text{ mm}^2$  for the former (MWCNT,  $\phi$ 13 nm) and the latter (MWCNT,  $\phi$ 67 nm), respectively.

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## 1. Introduction

Replacing synthetic rubber with natural rubber (NR) will significantly contribute to achieving low-carbon society. Currently, approximately 20,000,000 t of rubber materials are consumed worldwide, among which NR accounts for approximately 40%. The production energy required for NR is small, approximately only one-tenth of that for synthetic rubber. In addition, NR trees absorb approximately 90,000,000 t of  $\text{CO}_2$  per year [1]. Therefore, NR is considered to be precious natural resource. The application of NR is generally limited to temperatures of 60 °C or lower because of its low heat resistance and durability. However, NR composites filled with multi-walled carbon nanotubes (MWCNTs) can be used at temperatures up to 120 °C as previously reported [2]. The MWCNT/NR nanocomposites using fluorine-based rubber so far developed were applied for oil exploration and production [3], and demonstrated excellent mechanical properties [4,5]. A greater understanding of their electric conductivity [6] will widen their application scope and significantly promote the replacement of synthetic rubber with NR.

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Conductive rubber has been used as an electromagnetic-wave shield in devices, to prevent electrostatic discharge, and in planar heat-generating components [7–11]. The market size of conductive rubber is considered to be approximately 37 billion yen per year in Japan [12] and the range of application of conductive rubber as an electricity-conducting material is expanding. Types of conductive rubber include isotropic conductive rubber containing silicon (rubber contacts, keyboard switches, etc.), anisotropic conductive rubber (liquid crystal displays (LCDs) connectors, low-resistance connectors (printed-circuit boards, etc.), and pressure-sensitive conductive rubber (touch switches, sensors, etc.). Many researchers have reported on the constriction resistance at the electric contacts of metals, focusing on the shape of the contact surface since 60's [13], the studies of CNT [13–16] and CNT/NR composites [17–19] have progressed and also the studies of contact resistance of CNT/metal have started [20,21]. Recently, the research of conductive rubber as pressure sensors attracts attention [22–25]. For example, pressure dependence of the resistivity of conductive polymer is investigated because function of natural skin is established by transducing pressure into electronic signals in the field of robotics [23]. Thus, the development of innovative conductive rubber material is required. As noted above, the CNT/NR composite is a key material, being applicable for not only pressure sensors but also electronic devices such as switching

devices. This study investigated the contact resistance of CNT/NR nanocomposites for their application to switching devices.

## 2. Experimental

Natural rubber (SMR-CV60), Baytubes C70P (Bayer Material Science; mean diameter, 13 nm; length,  $\geq 1 \mu\text{m}$ ), MWNT7 (Hodogaya Chemical Co., Ltd.; mean diameter, 67 nm; length,  $\geq 7 \mu\text{m}$ ) and N330 high-abrasion furnace (HAF) carbon black (Tokai Carbon Co., Ltd.; mean grain size,  $\approx 28 \text{ nm}$ ) were used as the raw materials for preparing carbon/natural rubber (NR) nanocomposites. Three different nanocomposites, NR with Baytubes C70P (MWCNT-I), NR with MWNT7 (MWCNT-II) and NR with carbon black (CB) were prepared; hereafter, abbreviated as NR/MWCNT-I, NR/MWCNT-II and NR/CB. The fabrication procedures were as follows. One hundred grams of NR was rolled between two 6-in. open rollers separated by 1.5 mm with a speed ratio of 1.2 (24 rpm/20 rpm). It was expected that the molecular chains of NR were cut after applying a shear force for 5 min to decrease its viscosity and that free radicals were generated to promote the penetration of MWCNTs into the gaps of the NR and adhesion of NR to MWCNTs. The MWCNT powder was then mixed with the rolled NR, where the filler content was adjusted to 37.5 wt%, so as to result in the volume resistivity of  $10^{-2} \Omega \text{ m}$  order [6]. The obtained mixture was removed from the rollers, cooled to 10–20 °C, and passed five times between the two rollers with a reduced gap of 0.1 mm. The mixture was subjected to a large strain when passing between the two rollers but recovered to its original state immediately after passing between the rollers. By the repetition of such deformation and recovery, the MWCNTs were fibrillated and dispersed uniformly. The obtained mixture was then rolled between the two rollers with a gap of 1.5 mm for the second time. Two gram of dicumyl peroxide (DCP) was then added as a cross-linking agent, and the mixture was then rolled into a sheet of 1.2 mm thickness. The sheet was subjected to press curing at 175 °C for 20 min to obtain a cross-linked specimen. Sulfur cross-linking is generally selected for NR; however, peroxide cross-linking was adopted in this study because the heat resistance of sulfur-cross-linked materials is low [2,6].

The crystallinity of the MWCNTs was measured by Raman spectroscopy using a light with  $\lambda = 785 \text{ nm}$ . The extent of the dispersion of MWCNTs in the NR nanocomposites and the degree of adhesion of the MWCNTs with the NR were observed using a scanning electron microscope (SEM: Hitachi High-Technologies Corporation, SU8000) and a transmission electron microscope (TEM: JEOL, JEM-2200). The hardness of the NR nanocomposites was measured using a type-A durometer (Teclock Corporation, GS-719N) and determined as the mean of the hardness measured at five different points.

Fig. 1 shows the equipment of the measurement of the contact resistance. A brass-ball electrode of 8 mm diameter was plated with a nickel layer of 4  $\mu\text{m}$  thickness, which was then plated with a gold layer of 1.5  $\mu\text{m}$  thickness to decrease the resistance of the contact surface. A specimen was placed between this electrode and another brass-ball electrode to which a load of 2–200 g was applied to measure the current (mA) and voltage (V) at room temperature. The current was adjusted to 10 mA in this experiment.

## 3. Results and discussion

Fig. 2 shows surface SEM images of (a) NR/CB, (b) NR/MWCNT-I, (c) NR/MWCNT-II, and cross-section TEM images of (d) NR/MWCNT-I and (e) NR/MWCNT-II. The values of the hardness of

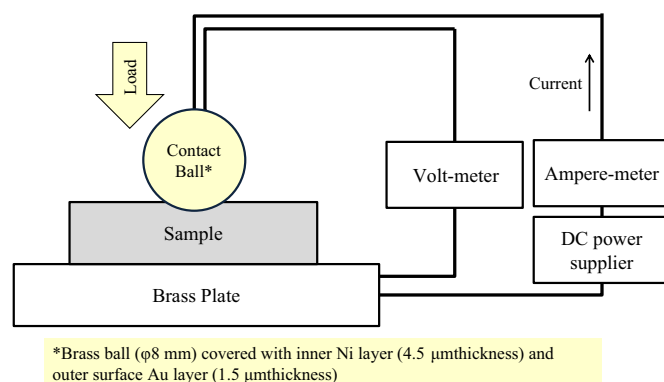


Fig. 1. Equipment for contact resistance measurement.

these specimens were also given in the SEM images. It can be noticed that many filler particles protrude from the matrix of MWCNT/NR (Fig. 2(b) and (c)), in contrast to CB/NR (Fig. 2(a)). The regions protruding from the matrix make up the contact area in the measurement. From this observation, MWCNTs were found to be uniformly dispersed in MWCNT-I/NR and MWCNT-II/NR. Fig. 2 (d) and (e) is observed interfaces of CNTs and rubber matrix for MWCNT-I/NR and MWCNT-II/NR, respectively. These TEM images suggest that CNTs are well fixed to rubber matrix. The hardness of the NR was 55 HsA, whereas those of the nanocomposites with CB, MWCNT-I and MWCNT-II were 72, 90 and 82 HsA, respectively. The value for MWCNT-I/NR was higher than that of MWCNT-II/NR. This observation is in good agreement with the report that the mechanical strength of MWCNT/NR having filler with a smaller particle diameter is higher than that with larger particle diameter [2]. Contrary to this relation, the hardness of CB/NR is less than that of MWCNT-II/NR whose particle diameter is larger than that of CB. In the case of MWCNT/NR, the three-dimensional cellular structure formed by MWCNT protects against deformation of the NR matrix [2]. This may be the reason why the hardness of MWCNT-II/NR is higher than that of CB/NR.

The Raman spectra of MWCNT-I and MWCNT-II were shown in Fig. 3. Both MWCNTs exhibited a strong G band at  $1580 \text{ cm}^{-1}$ . MWCNT-I showed a more intense D band at  $1350 \text{ cm}^{-1}$  relative to MWCNT-II. Therefore, a large number of entrapped defects near the surface of MWCNT-I/NR are expected to provide a greater number of reactive sites to bind with NR than in the case of MWCNT-II/NR [26,27]. As can be seen in Table 1, the electrical conductivity and mechanical strength of MWCNT-I/NR are higher than those of MWCNT-II/NR [2,6].

Fig. 4 shows the contact resistance plotted as a function of the load, where the data of CB/NR is not shown because it was unmeasurably large. The data for metal (brass plate) is also shown for comparison. At a load of  $\geq 100 \text{ g}$ , the contact resistance tends to saturate for MWCNT-I/NR and MWCNT-II/NR. The absolute value of the contact resistance of MWCNT-I/NR was higher than that of MWCNT-II/NR. However, these values are not enough low relative to that of brass. The dependence of  $R_c$  of MWCNT/NR on applied load was expressed in the formula,  $R_c = C \cdot P^n$  ( $P$ : load,  $C$  and  $n$ : constant): The equations derived from the least-squares method using experimental values are also shown in Fig. 4.

For metals that have been intensively studied in terms of the constriction resistance at the electric contacts, a relationship generally holds between the contact resistance ( $R_c$ ) and the load ( $P$ ) [13]. The contact resistance at electric contacts can be examined in terms of the stages (initial or latter) of the loading process, which correspond to different ranges of the exponent ( $n$ ) in the  $R_c$ - $P$  relationship. This similar examination was carried out for the MWCNT/NR in this study. The relationship between  $R_c$  and

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