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Glass Bead-Assisted Fine Dispersion of Multi-walled Carbon Nanotube in Silicone Matrix II: Effect on the Viscosity of Silicone Rubber†

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Electrically conducting silicone rubber composites were prepared by the incorporation of conducting fillers including carbon black, carbon fibers and carbon nanotubes. Silicon/multi-walled carbon nanotube (MWCNT) composites were produced by mechanical mixing. Glass beads (GBs) were introduced to significantly improve the dispersion of MWCNTs in the silicone matrix. The dispersion of MWCNTs in a silicone matrix is related to the ball-bearing effect of the glass beads. The electrical conductivity of the high viscosity-silicone/MWCNT/GB composite was approximately double that of the composite without glass beads due to the improved distribution uniformity of MWCNTs in the silicone matrix. In addition, the presence of glass beads in the silicone matrix improved the mechanical properties, such as the tensile strength and elongation at break as well as the electrical conductivity.

Key Words: Multi-walled carbon nanotube, High viscosity-silicone rubber, Glass bead, Mooney viscosity, Electrical conductivity.

INTRODUCTION

The electrical conductivity of polymer materials containing dispersing electrically conducting fillers, such as carbon black, carbon nanotubes or metal powders, was investigated[1-4]. These materials are used widely as contact point materials for electrostatic charge dissipation in a range of products, such as calculators, artificial organs, surface heaters, electromagnetic interference (EMI) shielding, rubber contact switches, *etc.*[5,6]. In most cases, silicone rubber is used as the polymer matrix of a conducting composite. The conducting silicone rubber composite has high resistance to weather and chemicals and can be used in a wide range of temperatures. In addition, the composite has excellent flexibility and the electrical resistance of the composite changes regularly with the external pressure[7,8]. On the other hand, carbon atoms are not compatible with silicon atoms and carbon materials of conducting fillers. In particular, multi-walled carbon nanotubes (MWCNTs) inevitably cause self-aggregation because of their high van der Waals force, surface area and high aspect ratio. Moreover, MWCNTs are insoluble in organic solvents due to the pure carbon element and its stable structure[9].

In a previous study[10], glass beads (GBs) were applied to improve the dispersibility of MWCNTs in the silicone matrix. The fine dispersion of MWCNT in the silicone matrix was caused by the ball-bearing effect of glass bead. The ball bearing effect was explained by an interfacial slip mechanism, as well as polymer chain disentanglement at the interface induced by high local shear between the nearby rotating glass bead spheres.

This study examined the effect of the viscosity of silicone rubber in the composite on the electrical percolation. In addition, the effects of the glass beads and the mixing time of the composite on the electrical percolation were assessed.

EXPERIMENTAL

Two types of silicone rubber (HR-1951UT and HR-1971UT) were obtained from HRS Co. Ltd., S. Korea. The multi walled carbon nanotubes (MWCNTs) were purchased from Hanwha Nanotech in S. Korea. The MWCNTs had a mean diameter of 10-20 nm and length of 10-50 mm. The glass beads (JFL-2000) were supplied by Binex Co. Ltd., S. Korea. The a-a'-di(*t*-butylperoxy) diisopropylbenzene (F-40, Mw : 338.5 g/mol, Seki Arkema, S. Korea) and trially cyanurate (TAC 50, Mw: 249 g/mol, Degussa, Germany) were used as a curing agent and curing co-agent, respectively. All the materials were used as received.

Preparation of silicone/MWCNT composite: Compounding of the silicone/MWCNT composite was accomplished using a double arm kneading mixer and a two-roll mill to

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incorporate the 0.3-3 phr MWCNTs, various amounts of glass beads, curing agent and curing co-agent. The compound was cured using a compression molding process at 170 ºC for 5 min and post-cured at 200 ºC for 2 h in a vacuum oven. Table-1 lists the compounding formulation for producing the silicone/MWCNT composites.

TABLE 1
COMPOUNDING FORMULATION FOR PRODUCING SILICONE/MWCNT COMPOSITES

	Set I	Set II	Set III
Silicone rubber (phr)	100	100	100
MWCNT (phr)	0.3/0.5/1/2/3	2	2
GB (phr)	-	-	10/30/50/100
Mixing time (min)	20	5/10/15/20/30	20

Characterization: A mechanical test (tensile strength, elongation at break and M100) was performed at ambient temperature using an Instron UTM (model 3345) at 500 mm/min. Dumbbell specimens were cut from 3 mm thick molded sheets. The electrical conductivity of the composites was measured using a Hiresta-UP MCP-HT450 (Mitsubishi Chemical Co., Japan). The Mooney viscosity test of the silicone/MWCNT composites was carried out using a Mooney Visco Meter (model DMV-200C, DAEKYUNG ENGINEERING Co. Ltd, S. Korea).

RESULTS AND DISCUSSION

Change in the viscosity of silicone rubber with various MWCNT loadings: Fig. 1 compares the HR 1951UT silicone rubber based composite with the HR 1971UT silicone rubber based composite as a function of the MWCNT loading. The Mooney viscosity of the original HR 1971UT silicone rubber was higher than those of HR 1951UT. The viscosity of the silicone/MWCNT composite increased with increasing MWCNT loading. In particular, above a MWCNT loading of 2 phr, the HR 1971UT silicone rubber/MWCNT composite showed a high viscosity. Therefore, the electrical properties of the HR1971 silicone with high viscosity and the MWCNT composite were investigated.

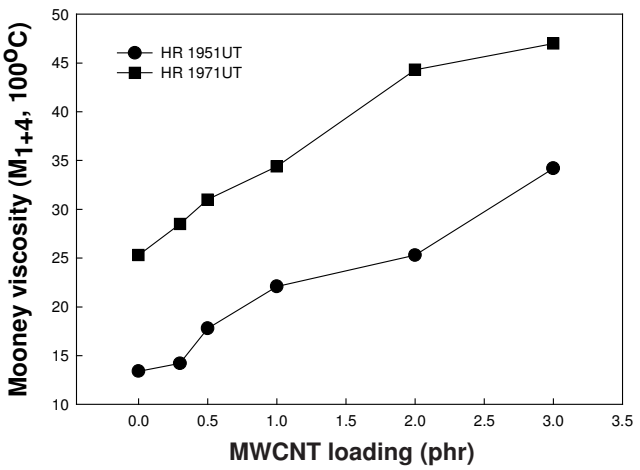

Fig. 1. Mooney viscosity of HR 1951UT based composite and HR 1971 UT based composite as a function of the MWCNT loading

Effect of MWCNT content: Fig. 2 shows the electrical conductivity of the composite with increasing MWCNT content. The electrical conductivity increased significantly between 1 and 2 phr. A previous study reported that HR 1951UT/MWCNT composites with 3 phr MWCNTs exhibited electrical percolation. On the other hand, the HR 1971UT/MWCNT composites showed electrical percolation at 2 phr MWCNT. Therefore, the electrical conductivity of the high viscosity silicone (below HV-silicone)/MWCNT composites was affected significantly by the viscosity of silicone rubber.

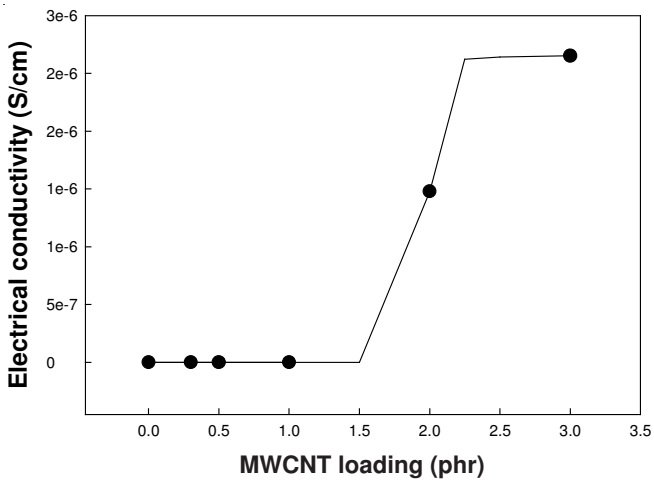

Fig. 2. Electrical conductivity of HV-silicone/MWCNT composites as a function of the MWCNT content (phr)

Effect of mixing-time of compounds with 2 phr MWCNT: Fig. 3 shows the electrical conductivity of HV-silicone/MWCNT(2 phr) composites according to the mixing time. The dispersibility of MWCNTs was improved between 15 and 20 min. The mixing time is important for achieving a fine dispersion of MWCNTs in silicone rubber.

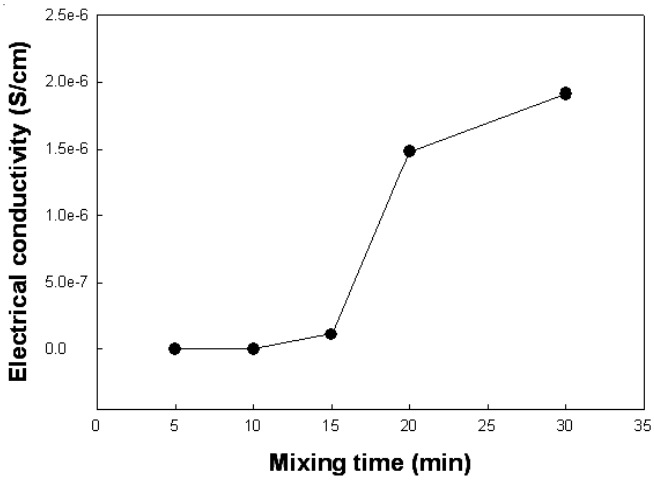

Fig. 3. Electrical conductivity of the HV-silicone/MWCNT(2 phr) composites as a function of the mixing time.

Effect of the amount of glass bead: The mixing time of the compounds was fixed to 20 min from the previous section, whereas different amounts of glass beads were added to the compounds to induce the ball-bearing effect. Fig. 4 shows the behaviour of the electrical conductivity of the composites with increasing glass bead content. The electrical conductivity improved between 10 and 30 phr. Therefore, the electrical

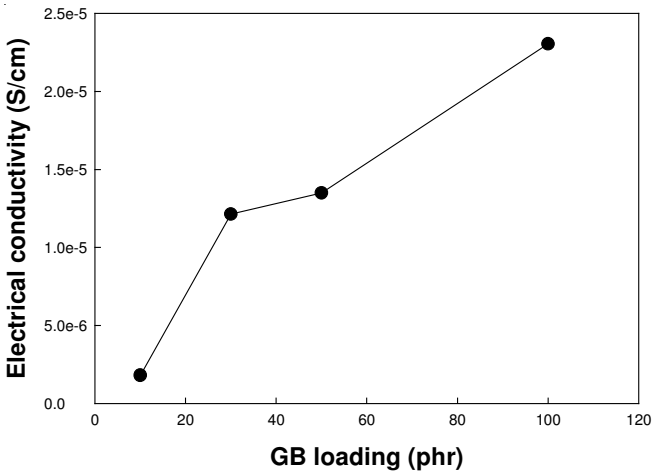

Fig. 4. Electrical conductivity of the HV-silicone/MWCNT(2 phr)/GB composites as a function of the mixing time

conductivity of HV-silicone/MWCNT/GB composite is affected significantly by the presence of glass bead in the compounds. Fig. 5 shows the mechanical properties (M100, tensile strength and elongation at break) of the HV-silicone/MWCNT(2 phr)/GB composites with various amounts of glass bead. The mechanical properties of the composites increased with increasing the amount of glass bead. For rigid particulate-filled polymer composites, in addition to the difference in modulus between the particles and polymer, some physical crosslinking points might be generated and the movement of the molecular chains of the polymer matrix would be restricted to some extent due to the addition of filler particles, leading to improved stiffness of the composites. On the other hand, in this study, the percolation content of glass bead was 30 phr, which means that the dispersibility of MWCNTs affected the viscosity of silicone rubber.

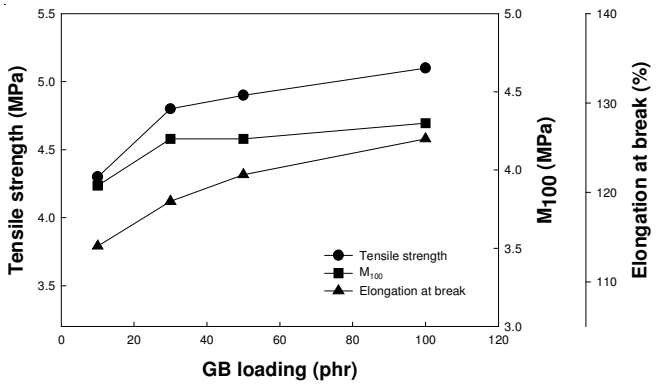

Fig. 5. Tensile strength, M100 and elongation of HV-silicone/MWCNT(2 phr) as a function of the glass bead loading at a 20 min mixing time

Morphology of the HV-silicone/MWCNT composites: Fig. 6 shows SEM images of the HV-silicone/MWCNT (2 phr) composites with different mixing times. MWCNT were observed on the surface of composite films after 5 min mixing. No MWCNTs were observed on the surface after a mixing time of 20min. Therefore, the dispersibility of MWCNTs improves with increasing mixing time.

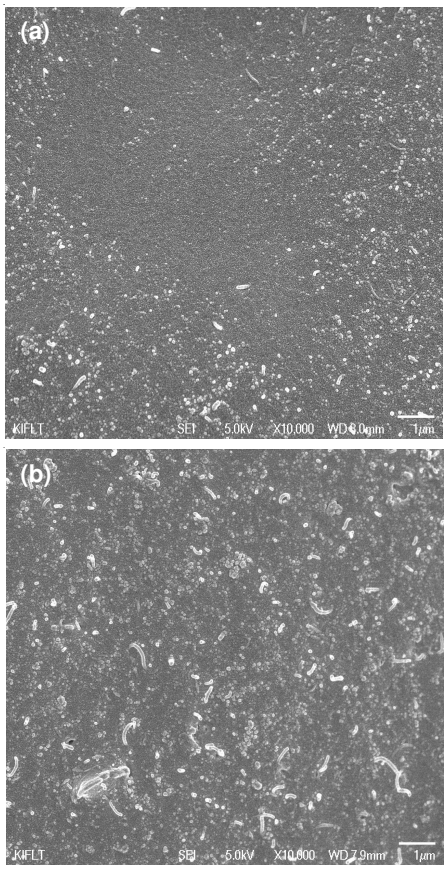

Fig. 6. SEM images of HV-silicone/MWCNT (2 phr) composites at different mixing time (a) 5 min, (b) 20 min

Conclusion

A previous study examined the effect of the mixing time of MWCNTs and the co-addition of glass beads in HV-silicone rubber composites. The present study examined the effect on the viscosity of silicone rubber in the composite on the electrical percolation. In addition, the effect of glass beads and mixing time of the composite on the electrical percolation was evaluated. Electrical percolation was observed with a MWCNT content of 2 phr. The HV-silicone/MWCNT(2 phr)/GB composite exhibited percolation at a 30 phr glass bead loading. Therefore, the viscosity of silicone rubber affects the dispersibility of MWCNTs in a silicone rubber matrix.

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