

Conducting Stability of Nickel-Coated Graphite/Methyl Vinyl Silicone Rubber Composites

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ABSTRACT: In this study, conductive composites of methyl vinyl silicone rubber (MVQ) filled with nickel-coated graphite (NCG) were prepared. The effects of the storage time, aging time, stretching, neutral-salt spraying, and acid-salt spraying on the electrical conductivity of NCG/MVQ were investigated. The results indicate that the values of the NCG/MVQ volume resistivity increased a little and were no greater than 0.1 Ω cm after long-term

storage, thermooxidative aging, stretching, and neutral-salt spraying, respectively; this showed good conductive stability. The volume resistivity rose rapidly under acid-salt spraying; this indicated poor conductive stability. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: conducting polymers; rubber; stabilization

INTRODUCTION

The development of the electronic information industry has created better lives for the people but has also brought a series of problems, including electromagnetic interference, leakage of electromagnetic wave information, and environmental pollution.¹ As a result, harm from electromagnetic radiation has attracted great attention. Nickel-coated graphite (NCG)/methyl vinyl silicone rubber (MVQ) composites not only have the advantage of low density, good aging resistance, and moderate cost, but their shielding effectiveness can also rival silver-based composites, which effectively reduce the harm produced from electromagnetic radiation.² Therefore, great advances in NCG/MVQ composites have been made in recent years.

Research on NCG/MVQ composites focusing on how to improve the mechanical properties and electrical conductivity has been undertaken by many researchers.^{3,4} However, there has been little study on the conductive instability of NCG/MVQ composites. This instability can be found during the storage process, transportation, installation, and use because of the great disparity between the interfacial properties of NCG and MVQ, which are inorganic and organic materials, respectively. In this study, we investigated the effects of the environments from long-

term storage, thermooxidative aging, tension (tensile strain and stretching numbers), and salt spraying (neutral-salt spraying and acid-salt spraying) on the stability of the conductive properties of NCG/MVQ to provided an effective guide for application.

EXPERIMENTAL

Materials

MVQ (grade 110-2, silica-containing) was obtained from Beijing Huaer Co., Ltd. (Beijing, China). The coupling agent, vinyltriacetoxysilane [A151, $\text{CH}_2=\text{CH}-\text{Si}-(\text{OOCCH}_3)_3$] was obtained from Beijing Reagent Chemical Corp. (Beijing, China). The vulcanizing agent, 2,5-dimethyl-2,5-bis(*tert*-butyl peroxy) hexane (DBPMH), was purchased from Qiangsheng Chemical Co., Ltd., China (Jiangsu Province, China). The crosslinking coagent, triallyl isocyanurate (TAIC), was bought from Liuyang Petrochemical Factory (Hunan Province, China). We prepared NCG by a carbonyl vapor-deposition process.⁵

Sample preparation

The compound formulations are given in Table I.

The NCG powder, coupling agent, and vulcanizing agent were blended in turn into MVQ by a two-roll mill (Guangdong Zhanjiang Machinery Factory, China). The blend was first vulcanized on a platen press (First Rubber Machinery Works, Shanghai city, China) under 10 MPa at 170°C for 20 min and then postvulcanized in a draught drying cabinet

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TABLE I
Formulation of the NCG/MVQ Composites

Ingredient	Formulation (phr)
MVQ	100
NCG	250
A151	10
DBPMH	2
TAIC	3

phr, parts per hundred of base polymer (parts of rubber in this study).

(DHG-9246A, Shanghai Jinghong Experiment Equipment Co., Ltd., Shanghai city, China) at 150°C for 4 h.

The NCG/MVQ vulcanized samples were cut to a size of 10 × 100 × 2 mm. The samples were tested after they were under the standard experiment conditions (23 ± 2°C, relative humidity = 50 ± 10%) for at least 16 h.

Test and characterization

The volume resistivity was tested by a direct-current bridge (QJ84, Shanghai Zhengyang Instrument Factory, Shanghai city, China) according to Chinese standard GB/T 2439-2001.

Hot-air aging of the samples was done in a thermal aging box (Tianjin Tianyu Experiment Instruments Co., Ltd., Shanghai city, China) according to Chinese standard 3512-2001.

Directional tension was applied with a homemade tension installation (Fig. 1). Five specimens per group were stretched to the designated strains, such as 0, 5, and 10%, and the volume resistivity was tested after 80 min.

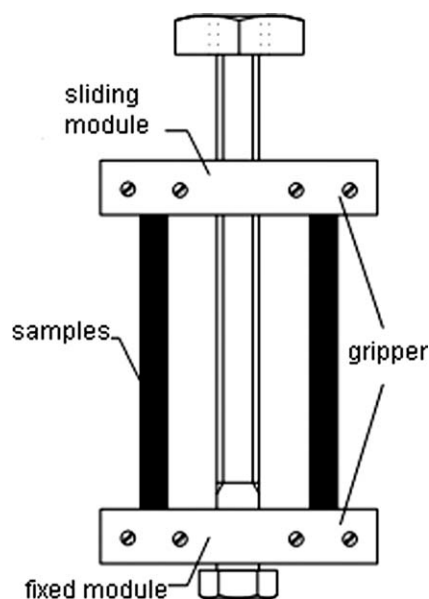


Figure 1 Oriented stretch experiment instrument that we designed.

TABLE II
Acid Seawater Formula in the Experiment

Material	Weight (g)	Material	Weight (g)
NaCl	27.2	K ₂ SO ₄	0.9
MgCl ₂	3.8	KBr	0.1
CaSO ₄	1.2	Na ₂ SO ₃	12.6
CaCl ₂	0.1	HCl (Analytical reagent)	20.3
MgSO ₄	1.7	H ₂ O	965

Repeated tensile experiments were carried out at a rate of 200 rpm on a rubber vertical fatigue tester (MZ-4003B, Jiangdu Pearl Test Machinery Plant, Jiangdu city, China). The volume resistivity was tested after the samples were left for 80 min.

The neutral-salt-spraying test was carried out in a salt-spraying cabinet (FQY-010A, Shanghai Huayan Instrument Equipment Co., Ltd., Shanghai city, China) according to Chinese standard GB 6458-86.

The acid-salt-spraying experimentation was carried out with a self-made device. Five bar samples per group were put in the acid-salt spraying device for 2, 4, and 7 days, respectively, and were then observed by scanning electron microscopy (S-4700, Hitachi Corp., Tokyo city, Japan), and finally, the volume resistivity was tested. X-ray photoelectron spectroscopy (XPS; ESCALAB 250, Thermo Fisher Scientific Corp., Massachusetts, USA) was the adjuvant used for analysis. SO₂ gas was dissolved into seawater, of which the salinity was 35% until saturation; this created the environment for acid-salt spraying. The formula of acid seawater is shown in Table II.

RESULTS AND DISCUSSION

Effect of the storage time on the conductive stability of the NCG/MVQ composites

It can take about 1 week, 1 month, or much longer to complete a cycle from manufacturing to

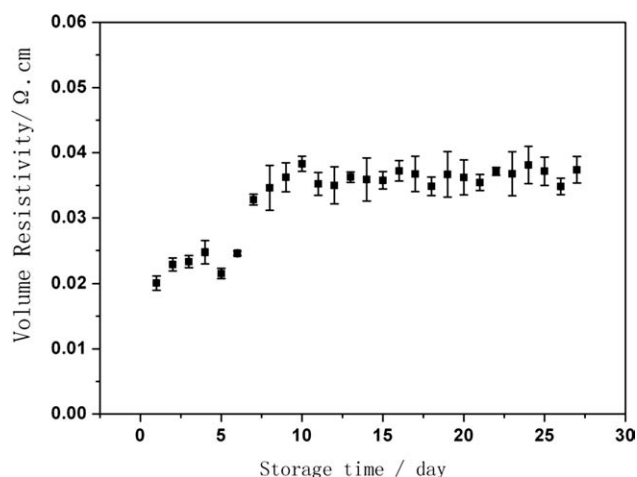


Figure 2 Effect of storage time on the volume resistivity of the NCG/MVQ composites.

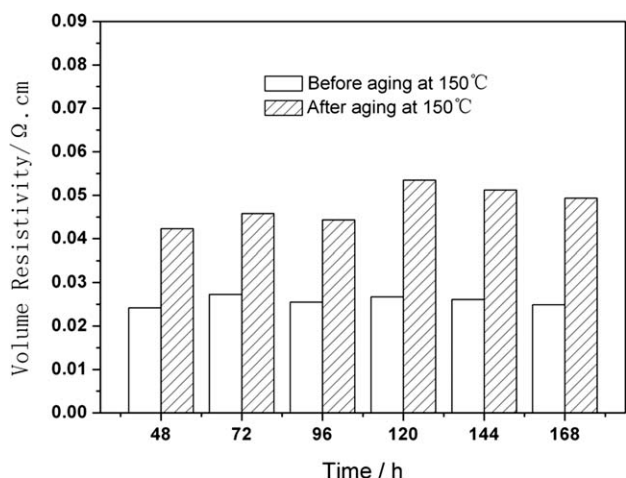


Figure 3 Effect of aging time on the volume resistivity of the NCG/MVQ composites.

marketing to usage for NCG/MVQ composites. To ensure the desired effect of the materials, in this study, we researched to the effects of storage time on the stability of the composites, as shown in Figure 2.

Figure 2 shows that the volume resistivity of the NCG/MVQ composites changed little as the storage time increased, and its value was 0.02–0.04Ω.cm. There was a slight increase after 10 days of storage, and a small change of around 0.035 Ω cm after 20 days. This may have caused by a rubber elasticity memory effect, in which the partial elastic deformation recovered slowly after vulcanization molding, although most elastic deformation was immobilized by crosslinking during curing. The recovery of deformation drove a little of the motion of the NCG particles. This led to an increase in the spaces between the particles or damage of the stiff network

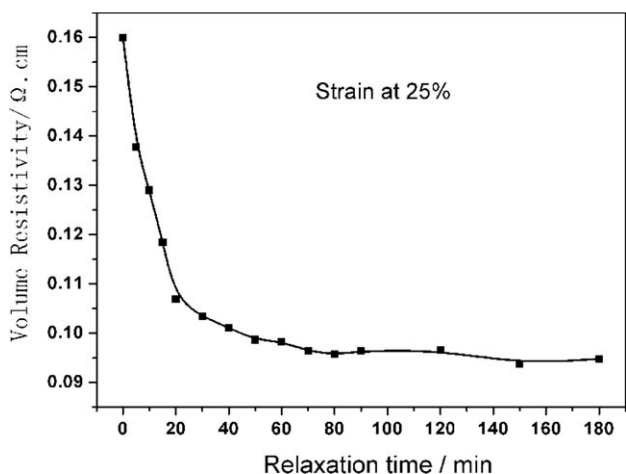


Figure 4 Effect of relaxation time on the volume resistivity of the NCG/MVQ composites.

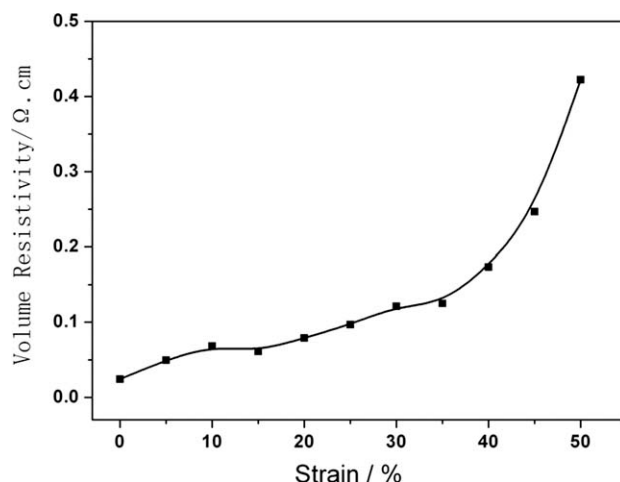


Figure 5 Effect of strain on the volume resistivity of the NCG/MVQ composites.

formed by conductive fillers, so the resistance increased in the first 10 days. With further increases in the storage time, the molecular chains of rubber had fully relaxed, and there was little effect on the conductive network; this resulted in good stability of the volume resistivity of the NCG/MVQ composites.

Effect of thermooxidative aging on the conductive stability of the NCG/MVQ composites

NCG/MVQ composites have been widely used in various fields, including navigation, medical treatment, and communication. It was necessary to investigate their conductive properties at high temperatures.

The volume resistivity of the NCG/MVQ composites was measured after thermooxidative aging at 150°C for 48, 72, 96, 120, 144, and 168 h, respectively. The results are shown in Figure 3.

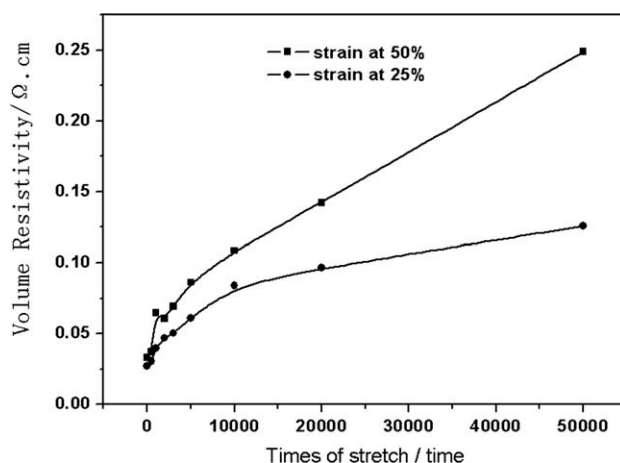


Figure 6 Effect of stretching times on the volume resistivity of the NCG/MVQ composites.

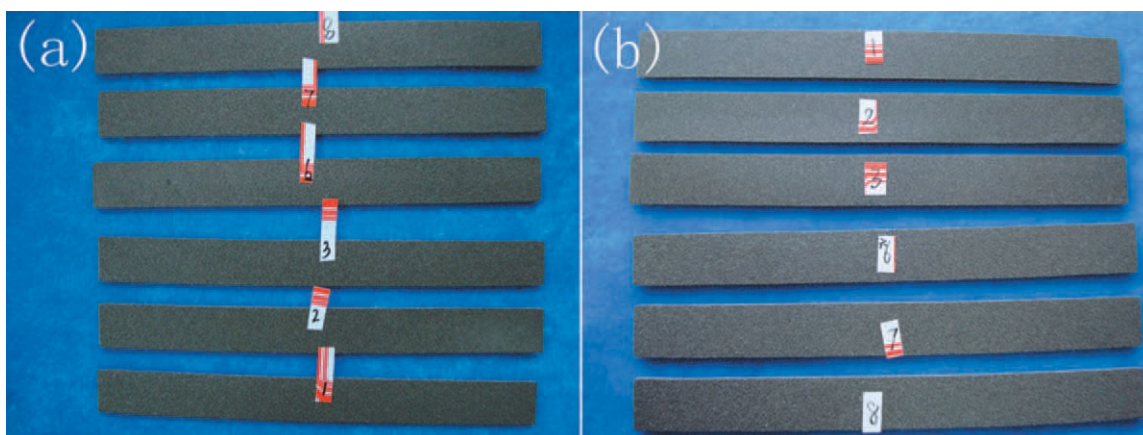


Figure 7 Changes of the NCG/MVQ samples (a) before and (b) after neutral-salt spraying. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The volume resistivity of the composites increased with aging time, and the values were all below $0.055 \Omega \text{ cm}$ with a slight variation. The increase in volume resistivity was due to the oxidation reaction on the surface of the conductive fillers at high temperatures, despite the fact that nickel has good stability at ordinary temperatures. The oxidation stopped after a dense oxide membrane was generated on the surface of nickel; this led to a small change in the conductivity, despite a prolonged aging time.

Effect of tension on the conductive stability of the NCG/MVQ composites

NCG/MVQ composites are often acted upon by some external forces, including stretching and bending; these cause changes in the inner structure of the composites, and then, the electric properties of the materials are affected further. So the effects of tensile strain and stretching times on the conductive stability of NCG/MVQ composites were researched in this study.

Effect of the tensile strain on the conductive stability of the NCG/MVQ composites

The motion of rubber molecular chains is time-dependent in that the relaxation time is needed for them to reach a steady state after a designated strain.⁶ Therefore, the values of resistance tested immediately are not accurate, whereas the values tested after a period of relaxation are the true results. The effect of the tensile strain on the volume resistivity of the composites was studied at a strain of 25%.

It is shown in Figure 4 that the change in the volume resistivity was very great from the beginning of relaxation (the relaxation time changed from 0 to 180 min). The volume resistivity decreased rapidly in 40 min, and after 70 min, it changed little. Thus, the values tested after a relaxation time of 80 min were the true resistances at the designated strain.

Figure 5 shows the relationship between the strain and volume resistivity of the NCG/MVQ composites. The volume resistivity of the NCG/MVQ composites increased with increasing strain. When the

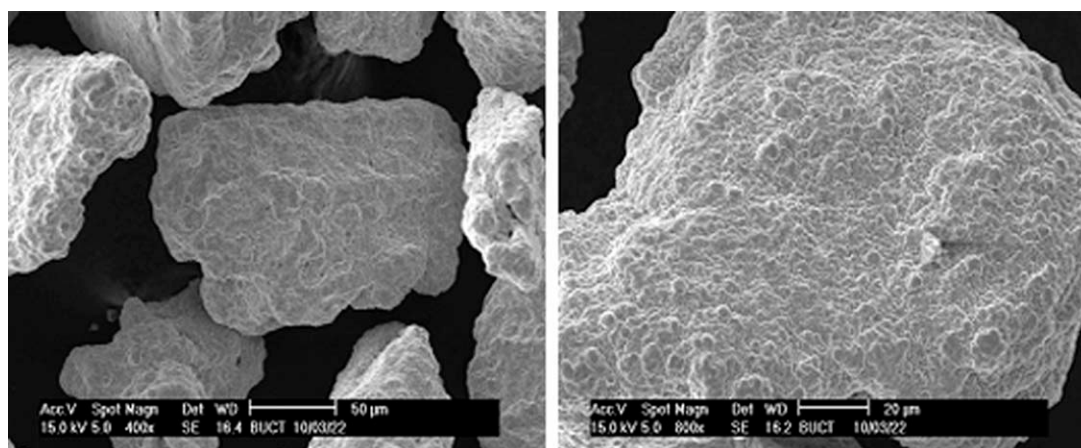


Figure 8 Surface conditions of NCG.

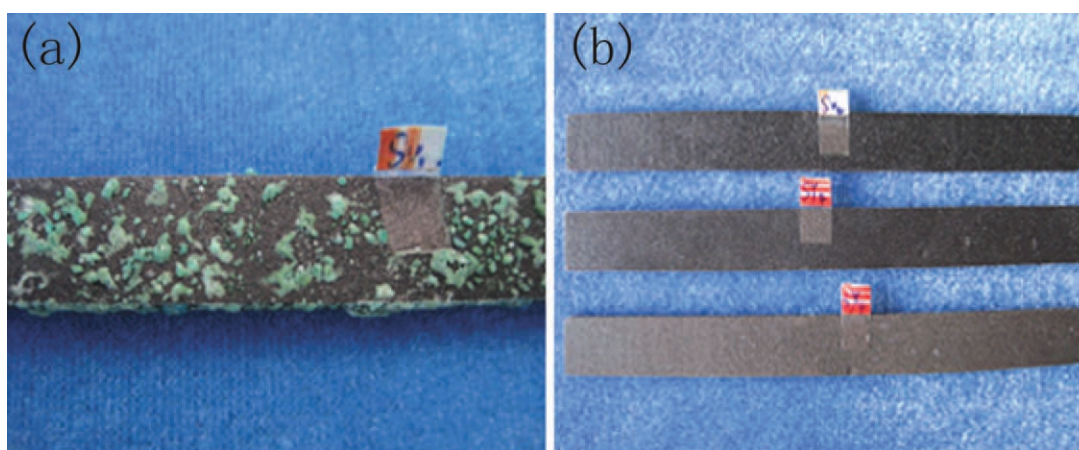


Figure 9 Changes of the NCG/MVQ samples after acid-salt spraying: (a) uncleaned sample and (b) cleaned samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

strain was over 35%, the volume resistivity increased conspicuously. When the materials had a little deformation, there was a small effect on the particle contact at small strains. When the strain was increased further, the distance of the fillers became large enough that the particles could not contact each other, so the conductive network was broken; this led to a rapid rise of volume resistivity. It is worth it to note that the composites retained fairly good electrical conductivity at strains of less than 25% (volume resistance $\leq 0.1 \Omega \text{ cm}$), so it presented important references for the installation and use of the composites.⁷

Effect of the stretching time on the conductive stability of the NCG/MVQ composites

Figure 6 shows the effect of the stretching times on the volume resistivity of the NCG/MVQ composites. The growth rate of the resistance of the composites

was fast at first and then stabilized as the stretching time was increased, and the volume resistivity of the sample that was deformed at a strain of 50% was obviously higher than that of the sample that was deformed at 25% with the same stretching times. The reasons for this were analyzed. The rapid increase in the space of the NCG particles and the great destruction of the conductive network at high strain led to the resistivity racing up. When the strain was fixed, however, the influence of the stretching time on the continuity of the conductive fillers was limited, and the rearrangement and orientation of the fillers that had a certain length-diameter ratio might have occurred, whereas the samples that were in the process of being oriented stretched repeatedly. As a result, the resistance of the composites changed slightly as the stretching times increased. After stretching for the same times, the greater the strain was, the more serious the destruction of the conductive network was, and the higher the volume resistivity of the composites was.

At a strain of 25%, the volume resistivity of the NCG/MVQ composites could be controlled ($\leq 0.1 \Omega \text{ cm}$) after they were stretched 20,000 times, whereas fewer than 5000 pulling times of the composites were needed to reach the same level of conductivity at a strain of 50%.

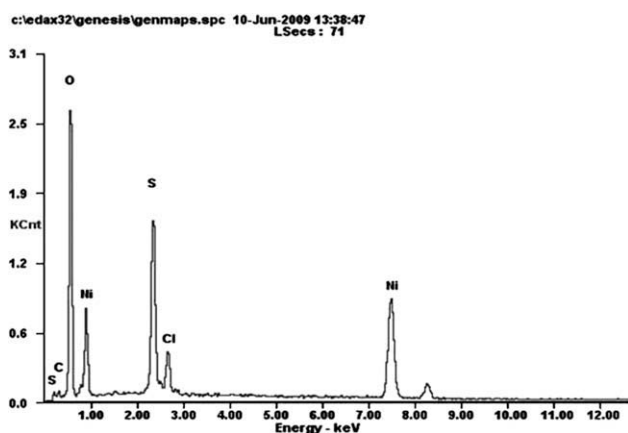


Figure 10 Energy spectrum analyses of the green particles in the NCG/MVQ sample surface.

TABLE III
Energy Spectrum Analysis of the Green Particles on the NCG/MVQ Sample Surface

Element	wt %	atom %
CK	05.80	11.77
OK	39.33	59.95
SK	13.08	09.95
CIK	03.57	02.46
NiK	38.21	15.87

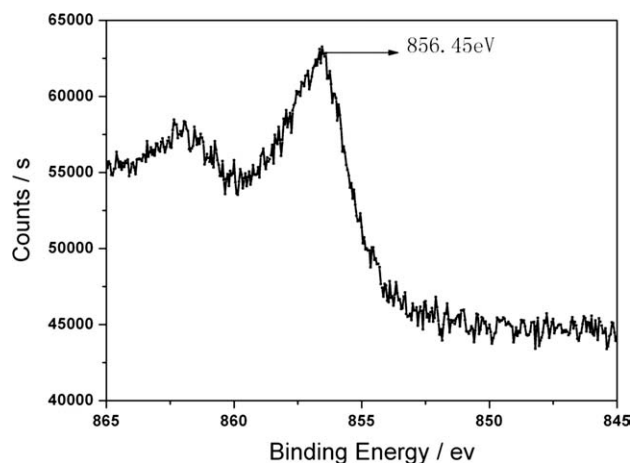


Figure 11 XPS analysis of the green particles on the NCG/MVQ sample surface.

Effect of salt spraying on the conductive stability of the NCG/MVQ composites

NCG/MVQ composites are widely used in ships and naval fleet electronic devices because of their reliable sealing properties and the good shielding effectiveness of silicone rubber. In the marine environment, metallic materials are susceptible to corrosion because seawater is a kind of electrolyte solution that influences the conductivity of composites. Therefore, the conductive stabilities of the NCG/MVQ composites in terms of neutral-salt spraying and acid-salt spraying were studied.

Effect of neutral-salt spraying on the conductive stability of the NCG/MVQ composites

We put the NCG/MVQ samples in a salt-spraying box for 2 days for aging at 35°C and then cleaned and dried them. The changes in the surface of the samples are shown in Figure 7.

There was no obvious difference in the NCG/MVQ samples shown in Figure 7(a,b), and no color

particles or lumps were found on the surface of the samples aged with neutral-salt spraying. The volume resistivity of the samples did not change a lot after aging and varied from 0.0141 to 0.0391 Ω cm. This was due to the conductive filler of NCG. The potential difference between materials that were immersed in electrolyte solutions was the chief driving force of corrosion. The more the potential difference was, the easier the materials were fretted. The conductive pathways of ions was another factor that led to corrosion.⁸ As the potential difference of the principal component of the conductive fillers (graphite and nickel) was small, the porosity of the compact was low, and the nickel coating was uniform with a high density (Fig. 8), so electrolyte solution ions were prevented from permeating the NCG fillers. Therefore, conductive pathways could not be formed, and corrosion was difficult. Also, the corrosion resistance of nickel is excellent. The NCG/MVQ composites possessed a high resistance to neutral-salt-spraying corrosion.

Effect of acid-salt spraying on the conductive stability of the NCG/MVQ composites

In the experiment using acid-salt spraying, we aged the NCG/MVQ samples for 2, 4, and 7 days, respectively, to further verify the corrosion resistance of the composites; this aging resulted in a visible alteration of the appearance of the samples, as shown in Figure 9.

There were a huge number of green particles on the surface of the NCG/MVQ samples without cleaning after acid-salt spraying, as shown in Figure 9(a). The color of the sample surface that was cleaned after acid-salt spraying became darker as the aging time increased [Fig. 9(b)]. We stripped the green particles off the sample surface and studied and analyzed them by energy spectrum analyses (Fig. 10); we found that the green particles were

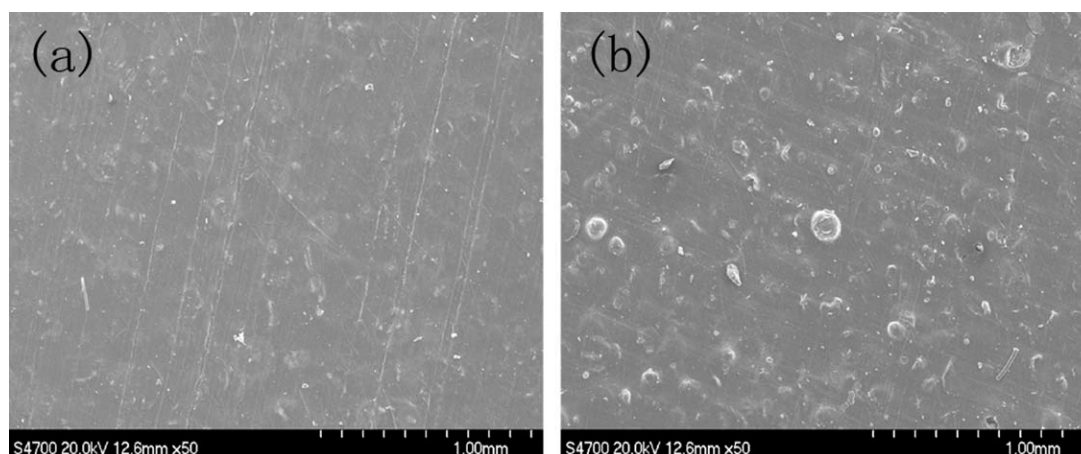


Figure 12 Microscopic change of the NCG/MVQ samples (a) before and (b) after acid-salt spraying.

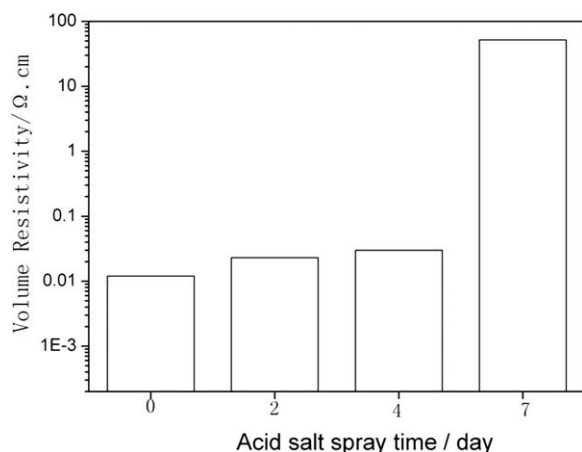
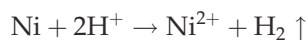


Figure 13 Effect of acid-salt-spraying time on the volume resistivity of the NCG/MVQ composite.

strongly impregnated with Ni, as Table III indicates. According to the results of XPS (Fig. 11), the peak position of Ni was found at a binding energy of 856.45 eV, which was beyond the scope of pure Ni (852.7–853.8 eV)⁹ and was very close to the binding energy of nickel sulfate, that is, 856.8 eV.^{10,11} So we speculated that the green granules were composed of a sulfate of bivalent nickel according to XPS and the color of the particles. In the environment of acid-salt spraying, the reaction took place on the surface of NCG:



As the bright nickel coating was corroded and then shed off, black graphite was exposed. Thus, the sample surface that was cleaned after acid-salt spraying turned out to be darker and darker as the aging time was increased. The pictures from scanning electron microscopy of the samples also verified this speculation.

Figure 12(a) shows that the sample surface was flat and smooth before acid-salt spraying. However, after the aging from acid-salt spraying, there were lots of filler particles exposed on the surface, which made it rough and uneven, and the nickel coating was visibly corroded, as shown in Figure 12(b).

Figure 13 shows the test results of the volume resistivity of the samples; these results indicate that the NCG/MVQ composites possessed poor resist-

ance to acid-salt-spraying corrosion. In the first 4 days, the volume resistivity of the NCG/MVQ composite samples increased slowly with acid-salt-spraying time and increased abruptly on the 7th day. The previous analysis showed that the change of the conductive network crossed by nickel–nickel with good electrical conductivity to graphite–graphite or graphite–nickel with poor conductivity, as a result of the peeling off of the corroded nickel by acid, caused the rapid rise of resistance in the NCG/MVQ composites.

CONCLUSIONS

In this study, we researched the effects of storage time, aging time, stretching, and salt spraying on the conductive stability of NCG/MVQ composites. The results show that the NCG/MVQ composites stored for long periods possessed great stability. The volume resistivity of the composites increased slowly with aging time, but the values are all below 0.1 Ω cm. The increases in the tensile strain and stretching time also induced an increase in the volume resistivity, and the composites retained a fairly good stability of electrical conductivity at a strain of less than 25%. The composites showed a high resistance to neutral-salt spraying, whereas poor stability was found under acid-salt spraying, which caused corrosion, and then, the volume resistivity of the NCG/MVQ composites increased rapidly.

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