

# Effect of Nanoclay on Electrical and Mechanical Properties of Polyurethane Conductive Coatings Filled with Nickel-Coated Carbon Fibers

S.A. Seyedmehdi, Hui Zhang, Jesse Zhu

Department of Chemical and Biochemical Engineering, Western University, London, Ontario, Canada

**There is a considerable amount of researches focused on the properties of nanocomposite containing nanoclays, yet there were only few studies about nanoclay conductive coatings. The influence of montmorillonite nanoclay on the electrical and mechanical properties of polyurethane conductive coatings filled with nickel-coated carbon fibers was investigated in this study. Moreover, the role of nanoclay with regard to the resistivity of coatings with different conductive fillers or different resins, the effects of resin to hardener ratio and mixing time on the resistivity and hardness of coatings were also evaluated. POLYM. ENG. SCI., 54:1120–1125, 2014. © 2013 Society of Plastics Engineers**

## INTRODUCTION

Conductive coatings are used in a variety of applications such as static dissipation, Electromagnetic interference shielding (EMI), and electrodes [1, 2]. For different applications, certain conductivities are required. For instance, antistatic coatings are used to bleed off triboelectric charge that may lead to spark and fire. They should have a surface resistivity between  $10^5$  and  $10^9 \Omega/\text{sq}$  in order to prevent sparking. Coatings for EMI shielding have surface resistivities less than  $10^5 \Omega/\text{sq}$  [3]. Conductive coatings are usually made by incorporating conductive fillers in organic polymer film forming materials. Conductive polymers such as polyaniline and polypyrrole have also been used in conductive coatings, but their applications were limited because of poor processability and high cost [4]. Most frequently used conductive fillers are graphite, carbon black, and metallic powders.

One of the important factors affecting the conductivity of coatings is filler fraction. Conductive coatings indicate conductivity only when the filler fraction in the coatings reaches to the point that is known as percolation threshold. This is a point when the particles contact each other and a continuous path is established through which elec-

trons can pass [5, 6]. For most applications, it is beneficial to reduce the percolation threshold so as to decrease the cost and improve the mechanical properties of conductive coatings.

Nonconductive clay nanofiller (intercalated montmorillonite) has been applied over the last 10 years to design nanocomposites that have shown better mechanical, thermal, and barrier properties compare to usual composites [7–10]. Montmorillonite is a member of smectite clays and the particles are plate-shaped with an average diameter of approximately  $1 \mu\text{m}$ . It has an unusually high aspect ratio that can improve composite properties. During the dispersion of nanoclay in polymers, gallery spaces can be filled with polymer. The clay is swollen when the distance between platelets increases. The clay platelets that are swollen by polymers are intercalated. Exfoliate happens when clay swells so much that it is no longer organized in stacks and nanocomposites show the best properties in this structure [11]. Nanoclay has been also used in conductive composites containing carbon black to improve the dispersion of pigment in polymer matrix and to reduce the percolation threshold [12]. However, further reports on the effects of nanoclay on the dispersion of conductive pigments are scarce and more in-depth evaluations are needed. This study investigated the effect of nanoclay on electrical and mechanical properties of polyurethane conductive coatings with nickel-coated carbon fibers (NCF). Furthermore, the influences of resin-to-hardener ratio in resistivity and mechanical properties of conductive coatings with nanoclay were studied. In order to find out the effects of different types of conductive fillers, nickel-coated graphite was also tested.

Graphite has a layered, planar structure that each layer includes carbon atoms that are arranged in a hexagonal lattice. It can conduct electricity as it has enormous electron delocalization within the carbon layer and these electrons can move freely, so they are able to conduct electricity. However, graphite can only transfer electricity through the plane of the layers [13].

Micron-sized carbon fibers include at least 90% carbon and are prepared by heat treatment or controlled pyrolysis of different precursor fibers. A bundle of many thousands

Correspondence to: Dr. Hui Zhang; e-mail: hzhang1@uwo.ca

DOI 10.1002/pen.23656

Published online in Wiley Online Library (wileyonlinelibrary.com).

© 2013 Society of Plastics Engineers

TABLE 1. The material characterization of nickel coated carbon fibers.

Nickel	60%
Apparent density	1.8 g/cm <sup>3</sup>
Screen analysis	95%–120 $\mu$ m

of carbon filaments make carbon filament thread that has diameter of approximately 5  $\mu$ m. The atomic structure of carbon fiber is similar to the graphite while the sheets in carbon fibers interlock. Graphite or carbon fiber may be used in combination with metallic powders to reduce their costs. For instance, nickel-coated graphite is produced from graphite powder, which has been completely encapsulated with a layer of high purity nickel by the carbonyl decomposition process [13].

## EXPERIMENTAL

### Materials

The polyol (Desmophen A-160 SN) and its Polyisocyanate (Desmodure N75-BA) hardener used in this work were obtained from Bayer Company. The hydroxyl content of Polyol was 100 mg KOH/g and NCO% of Polyisocyanate was 16.5%. Also, NCF (E-Fill 2901, Sulzer Metco Company), nanoclay (Southern Clay Products), and solvents (MEK and Toluene) were used in this study.

Nickel-coated graphite (Novamet Company), epoxy resin (Araldite GZ471-X75, Huntsman Company), and its polyamine hardener (Aradur 283, Huntsman Company) were also used to evaluate the effect of conductive filler and resin type on the electrical resistivity of nanoclay conductive coatings.

Tables 1 and 2 indicate the typical properties of NCF and nickel graphite, respectively.

### Preparation Method

Polyol was mixed with NCF, nanoclay, and solvent in a lab scale ball mill (Gardco Company, USA) containing ceramic beads for 3 hours. The final dispersion and polyisocyanate as hardener were homogeneously mixed together by a stirrer (the ratio of polyol to hardener was 4 to 1). Two different nanoclays were used: the first clay had a mean particle size of 25  $\mu$ m (A) and the second one had a mean particle size of 5  $\mu$ m (B). Nanoclay was added in concentrations of 2–8 wt% to polyurethane coatings with 35 wt% NCF or nickel-coated graphite (the percolation threshold of these two fillers in conductive coating was 30 wt%). Final coatings were applied by compressed air spray gun on glass substrate and cured at

room temperature. The thickness was controlled between 40 and 50  $\mu$ m. The electrical test and hardness were conducted two days after curing.

### Surface Resistivity

The surface resistivity of coatings [14] was tested by using a surface resistivity meter (Four Probes Tech Company, China). This method uses probes aligned linearly that contact the surface of the material being tested. For each sample, the resistivities were checked in five different spots and their average was reported.

### Hardness

Pencil test [15] was employed to measure the hardness of coatings. A set of calibrated wood pencils with different hardness was used in which the softest was 6B and the hardest was 6H.

### Surface Morphology

A scanning electron microscopy (SEM) equipped with EDX, Hitachi S-2600 (Hitachi, Pleasanton, CA), was utilized to compare the cross-section structure of nanoclay conductive coatings with NCF and nickel-coated graphite. All samples were gold-sputtered before scanning.

### Method for the Evaluation of Nanoclay Effect on Dispersion of Conductive Filler

The effects of nanoclay on conductive filler dispersion in coating films were investigated by EDX analysis of conductive coating cross section (with NCF and 6 wt% nanoclay). The fraction of nickel was measured in three different areas of the coating cross-section: (1) top of the coating (Area 1), (2) in the bulk of coating (Area 2), and (3) near the substrate (Area 3). Because the resistivity of conductive coatings is directly affected by the dispersion of conductive filler, the effects of nanoclay on the dispersion of E-fill 2091 were analyzed by the film resistivity.

## RESULTS AND DISCUSSION

### Polyurethane Conductive Coatings with Nanoclay

Figure 1 indicates the resistivity changes of conductive coatings containing NCF with different nanoclay fractions. As it can be seen, nanoclay can reduce the resistivity of coatings and this reduction is more considerable with nanoclay (A) that has larger particle size than that of (B). For both nanoclays, there were not considerable resistivity reductions when the nanoclay fraction increased to more than 6 wt%.

Nanoclay could affect the resistivity of coatings in two ways. Firstly, it improves the dispersion of conductive fillers in the coatings [11], but nanoclay (B), with smaller

TABLE 2. The material characterization of nickel graphite.

Nickel	60%
Apparent density	1.4–1.5 g/cm <sup>3</sup>
Screen analysis	95%–100 $\mu$ m

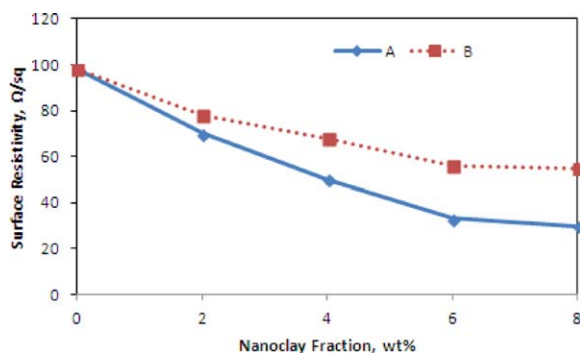


FIG. 1. The effect of nanoclay fraction on the resistivity of conductive coating. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

particle size, could not be well dispersed as the larger nanoclay (A) and therefore, it could not help the dispersion of conductive filler as well as nanoclay (A). Secondly, nanoclay has some ions in its structure that could develop the movement of electrons in conductive coatings [12]. The relatively poorer dispersion of nanoclay (B) would restrict the electron movement between nanoclay and conductive fillers. The results are in agreement with the finding of other researchers that the dispersion of solid particles in polymer is more difficult when the particle size reduces [14, 16, 17].

Table 3 compares the distributions of nickel concentrations across the thickness of coating film with larger nanoclay (A), smaller nanoclay (B), and without nanoclay (D). The addition of nanoclay significantly improved the distribution of E-fill 2091. Furthermore, the larger size nanoclay was more effective in promoting a uniform overall distribution of E-fill 2091.

The nanoclay had high aspect ratio and could improve the hardness of coatings. As it can be found in Table 4, the conductive coating hardness improves with increasing

TABLE 3. Nickel distributions in conductive coatings (Nanoclay fraction: 6 wt%, Conductive filler fraction: 35 wt%).

	Nickel fraction wt%		
	A	B	D
Area 1 (Top)	11.6	7.5	5.6
Area 2 (Bulk)	13.7	10.8	8.5
Area 3 (Near substrate)	9.6	14.9	19.6

TABLE 4. The change of coating hardness with nanoclay fractions.

Nanoclay fraction (wt%)	Hardness (with nanoclay A or B)
0	3H
2	3H
4	3H
6	4H
8	4H

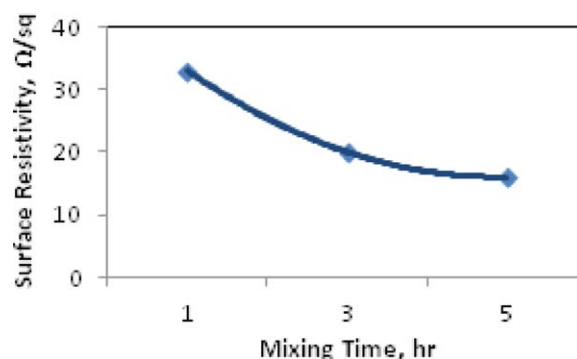


FIG. 2. Surface resistivity of nanoclay conductive coating against mixing time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nanoclay fraction and the two nanoclays showed no difference in hardness improvement.

The comparison of results for nanoclay conductive coatings containing small and large size nanoclay determined that larger size could reduce the surface resistivity more. Therefore, the larger size (25  $\mu\text{m}$ ) nanoclay was used, in this study, to evaluate the effects of mixing time, resin-to-hardener ratio, conductive filler and resin type on the electrical property, and hardness of conductive coatings.

#### *The Effect of Mixing Time on Nanoclay Conductive Coating*

As it was mentioned before, conductive coating was homogenized in a ball mill. The time of mixing was changed from 1 to 5 hours to evaluate the effect of mixing time on the electrical property and hardness of conductive coating containing 6 wt% nanoclay (A) and E-fill 2091. As it can be found in Fig. 2, the resistivity of conductive coatings was reduced with increased mixing time.

When the mixing time was increased, the dispersion of coating improves and therefore the surface resistivity reduces. The results also show that there is not a significant change in the aspect ratio of carbon fibers that may happen in the ball milling of coatings. The breakdown of carbon fibers can reduce the conductivity and has been reported by some researchers [16, 17].

Furthermore, Table 5 demonstrates the hardness changes of conductive coatings with different mixing times. The results verified that hardness increases with increased mixing time. As a result, both the electrical and

TABLE 5. The hardness changes of conductive coating against mixing time (Nanoclay: 6 wt%; conductive filler: 35 wt%).

Mixing time (h)	Hardness
1	3H
3	4H
5	4H

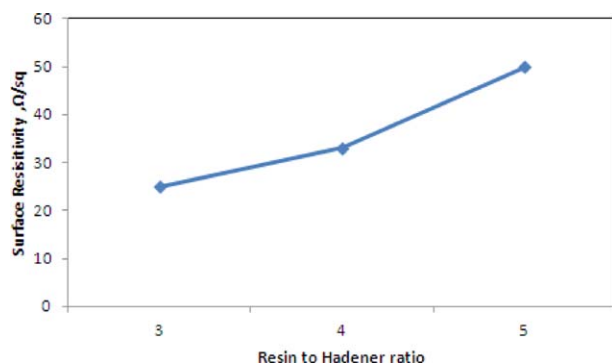


FIG. 3. Surface resistivity of conductive coating against resin/hardener ratio. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

mechanical properties of conductive coatings with nanoclay were improved, when the mixing time increased.

#### *The Effect of Resin to Hardener Ratio on Conductive Coating Properties*

The ratio of polyol resin to isocyanate hardener was varied from 3/1 to 5/1 in conductive coating containing E-fill 2091 and 6 wt% nanoclay. The stoichiometry of resin/hardener was 4/1. Figure 3 indicates the alteration of resistivity with resin to hardener ratios.

The results displayed that when the hardener amount in nanoclay conductive coating reduced, the surface resistivity increased. This phenomenon can be explained by the coating shrinkage. More hardener (in a certain range) added to the system would normally promote better cross-linking and produce a more consolidated coating film. This would in turn make conductive particles get closer to each other and finally produce a reduced surface resistivity [16].

The comparison of conductive coatings hardness with nanoclay in different resin to hardener ratios determined that with increasing the resin/hardener ratio, the coating hardness would decrease. Table 6 shows the hardness of conductive coatings with nanoclay in different resin/hardener ratios.

It can be found from the results that the resin/hardener ratio can affect both the electrical and mechanical properties of conductive coating with nanoclay and there is an optimal ratio of resin/hardener that good mechanical and electrical properties can be achieved.

TABLE 6. The hardness changes of conductive coating in different resin/hardener ratio (Nanoclay: 6 wt% conductive filler: 35 wt%).

Resin/hardener ratio	Hardness
3	4H
4	4H
5	3H

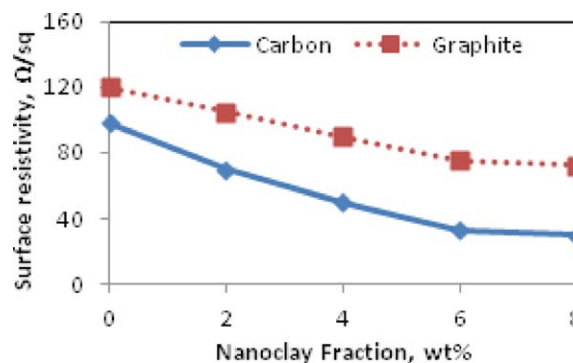


FIG. 4. The changes of surface resistivity for two different conductive coatings against nanoclay fraction. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

#### *The Effect of Conductive Filler Type on Conductive Coating*

Two different conductive fillers, NCF and nickel-coated graphite were used in this study. The mixing times of both conductive fillers with Polyol were 3 hours. Figure 4 illustrates that the surface resistivities of both conductive coatings with NCF and graphite reduced with increasing nanoclay (25  $\mu\text{m}$ ) fractions from 2 to 8 wt% and the optimal nanoclay fraction was attained between 6 and 8 wt%. However, the lowest surface resistivity was obtained with carbon fibers.

The lower surface resistivity of the coating made from carbon fibers might be attributed to the higher aspect ratio of them, which benefits the electron transfer in coatings.

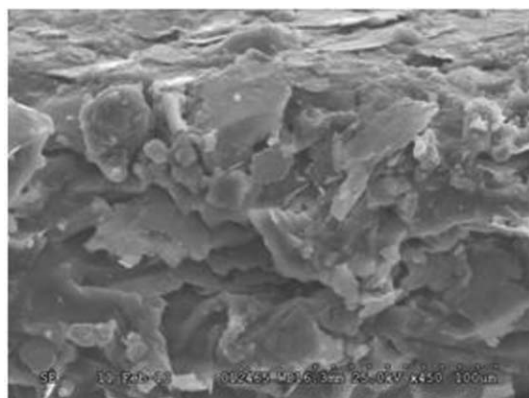
SEM pictures were employed to investigate the effect of conductive filler type on surface resistivity of conductive coatings with nanoclay. Figure 5 compares the cross-sectional SEM pictures of conductive coating films with nickel-coated graphite (S1) and carbon fibers (S2). The results proved that coatings with carbon fibers have a different structure than that of graphite. The amorphously oriented carbon fibers structure could develop better conductivity of coatings than graphite because carbon fibers can contact each other better [13, 16].

Table 7 indicates the conductive coatings hardness in different nanoclay fractions. The higher coating hardness with carbon fiber against graphite might be related to the structure of carbon fiber, which had a higher strength than graphite, so it could improve the hardness of conductive coatings.

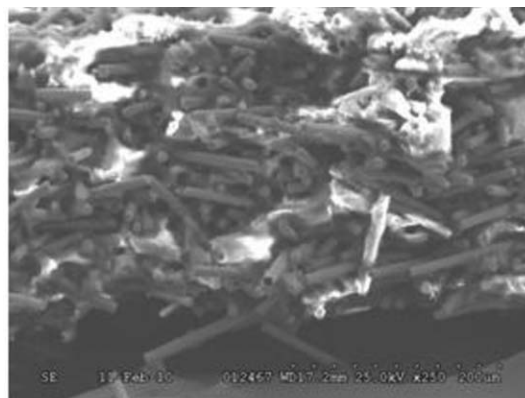
#### *The Effect of Resin Type on Conductive Coating Properties*

Another resin, epoxy, was also employed to produce conductive coatings, in order to evaluate the effects of resin type and nanoclay fraction on the electrical property and hardness of coatings. Both of the two different conductive coatings (polyurethane and epoxy) were incorporated with NCF. Figure 6 shows that the surface resistivities of both polyurethane and epoxy conductive





S1. Conductive coating with nickel coated graphite



S2. Conductive coating with nickel coated carbon fibers

FIG. 5. Cross-sectional SEM pictures of two different conductive coatings with graphite (S1) or carbon fibers (S2).

coatings reduce with increasing nanoclay (25  $\mu\text{m}$ ) fractions. However, the reduction in polyurethane conductive coating was more considerable than in epoxy conductive coating. The optimal point for both coating was attained between 6 and 8 wt% nanoclay in either case.

As it can be observed in Table 8, the hardness of polyurethane (PU) conductive coating is higher than epoxy conductive coating. However, nanoclay could increase the hardness of both conductive coating (epoxy and polyurethane) with NCF.

The comparison of polyurethane and epoxy conductive coatings with nanoclay showed that the type of resin could influence the electrical properties of nanoclay conductive coatings. The difference may be related to the structure of epoxy and polyurethane resins. The epoxy resin has a semi-crystalline structure, whereas the polyurethane resin has an amorphous arrangement and conductive particles can contact better in the second structure [16].

## CONCLUSION

The influence of nanoclay on the electrical property and hardness of polyurethane conductive coatings with NCF was investigated. In addition, the effects of resin to hardener ratio, mixing time, conductive filler type and

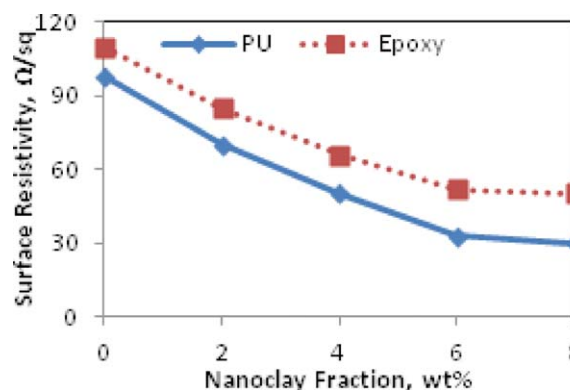


FIG. 6. The effect of nanoclay fraction on the surface resistivity of polyurethane and epoxy conductive coating. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

resin type on the electrical property, and hardness of nanoclay conductive coating were evaluated. The results indicated that nanoclay could improve the conductivity of polyurethane conductive coatings containing NCF. The optimal fraction of nanoclay was achieved between 6 and 8 wt%. Also, the mixing time and resin to hardener ratio could affect the electrical property and hardness of nanoclay conductive coatings. The optimal mixing time was

TABLE 7. Hardness changes of conductive coatings (carbon fiber and graphite) against nanoclay fraction (conductive filler: 35 wt%).

Nanoclay fraction (wt%)	Hardness	
	Carbon fiber	Graphite
0	3H	2H
2	3H	2H
4	3H	3H
6	4H	3H
8	4H	3H

TABLE 8. Hardness changes of conductive coatings (PU and Epoxy) against nanoclay fraction (conductive filler: 35 wt%).

Nanoclay fraction (wt%)	Hardness	
	PU	Epoxy
0	3H	2H
2	3H	2H
4	3H	3H
6	4H	3H
8	4H	3H

between 3 and 5 hours and the lowest resistivity was attained at resin to hardener ratio 3/1. The comparison of nanoclay conductive coatings with NCF and with nickel-coated graphite, respectively, indicated that nanoclay has a more significant influence on conductive coatings with carbon fibers. Also, nanoclay demonstrated better electrical property and higher hardness with polyurethane coatings when compared with epoxy coatings. In summary, nanoclay could decrease the cost and improve the electrical property and hardness of conductive coatings.

## REFERENCES

1. Z.-H. Chen, Y. Tang, F. Yu, J.-H. Chen, and H.-H. Chen, *J. Coat. Technol. Res.*, **5**, 259 (2008).
2. B. Lee, W. Woo, and H. Park, *J. Mater. Sci.*, **37**, 1839 (2002).
3. S. Syed Azim, A. Satheesh, K.K. Ramu, S. Ramu, and G. Venkatachari, *Prog. Org. Coat.*, **55**, 1 (2006).
4. D. Zhao, Q. Lei, and C. Qin, *Pigm. Resin Technol.*, **35**, 341 (2006).
5. C. Zhang, X.-S. Yi, H. Yui, S. Asai, and M. Sumita, *J. Appl. Polym. Sci.*, **69**, 1813 (1998).
6. J.F. Feller, I. Linossier, and G. Levesque, *Polym. Adv. Technol.*, **13**, 714 (2002).
7. X. Fu and S. Qutubuddin, *Polymer*, **42**, 807 (2001).
8. X. Fu and S. Qutubuddin, *Mater. Lett.*, **42**, 12 (2000).
9. K.E. Strawhecker and E. Manias, *Chem. Mater.*, **12**, 2943 (2000).
10. G. Chen, X. Chen, Z. Lin, W. Ye, and K. Yao, *J. Mater. Sci Lett.*, **18**, 1761 (1999).
11. J.A. Johnson, M.J. Barbato, S.R. Hopkins, and M.J. O'Malley, *Prog. Org. Coat.*, **47**, 198 (2003).
12. J.F. Feller, S. Bruzaud, and Y. Grohens, *Mater. Lett.*, **58**, 739 (2004).
13. Xanthos, "Functional Fillers for Plastics", Wiley-VCH (2005).
14. ASTM D4496-04.
15. ASTM D3363-05.
16. J. Pionteck and G. Wypych, "Handbook of Antistatics", Chem Tech Publishing, Toronto (2007).
17. P. Vandervorst, C.H. Lei, Y. Lin, O. Dupont, A.B. Dalton, Y.P. Sun, and J.L. Keddie, *Prog. Org. Coat.*, **57**, 91 (2006).