An Electrical Approach to Monitor Wire and Cable Thermal Oxidation Aging Condition Based on Carbon Black Filled Conductive Polymer Composite

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ABSTRACT: Polymeric materials are widely used as insulation and jacketing materials in wire and cable. When such materials are used for long-term applications, they undergo thermal oxidation aging in the environment. It is necessary to develop an *in situ* and nondestructive condition monitoring (CM) method to follow the aging of cable materials. The main objective of this work was to investigate low-density polyethylene/carbon black (LDPE/CB) conductive polymer composites as potential sensor materials for this purpose. LDPE/CB composites with a carbon black loading below the percolation threshold underwent accelerated thermal oxidation aging experiments. The results indicated that the substantial resistivity decreases of the LDPE/CB composites could be directly related to the increases in volume fraction of the conductive carbon black, which was mainly caused by the mass loss of polymer matrix and sample shrinkage during the thermal oxidation aging process. Compared to existing CM method based on density change, the electrical resistivity is more explicit regarding its absolute changes throughout the thermal oxidation aging. The change in resistivity spanned over four orders of magnitude, whereas the composite density only increased 10%. The results offer strong evidence that resistivity measurements, which reflect property changes under thermal aging conditions, could represent a very useful and nondestructive CM approach as well as a more sensitive method than density CM approach. Crystallinity changes in materials investigated by modulated DSC and TGA measurements indicated deterioration of crystalline regions in polymer during the thermal oxidation aging. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 513–520, 2004

Key words: polyethylene; carbon black; conductive polymer composite; electrical properties; crystallization

INTRODUCTION

Wire and cable integrity is critical to the safe and reliable operation of nuclear power plants. The polymeric materials used in wire and cable insulation and jacketing degrade with aging at service, especially in severe environmental conditions. Consequently, it demands for both existing and future nuclear power plants to monitor the insulation polymers to anticipate material degradation before the performance of wire and cable is adversely affected. ANSI/IEEE Standard 383 requires aging studies to establish a long-term performance of wire and cable insulation for use in nuclear power stations.[1]

Several methods were developed to monitor the aging condition of wire and cable materials, for example, (1) Tensile strength and elongation at break testing[2]: These two parameters are found to be the most direct and useful indicators of the remaining mechanical properties. A general consensus in industry is that a retained elongation at break of at least 50% absolute value of the materials would be satisfactory for continued service; (2) Density testing[3]: cable materials such as ethylene–propylene rubber (EPR) experience an increase in density with aging, and density data related to accelerated thermal aging of some polymers have been reported; (3) Oxidation induction time (OIT) testing[4]: OIT evaluates the relative amount of antioxidants remaining in the materials. Materials at an advanced stage of degradation have OITs on the order of a few minutes; (4) Indenter modulus testing[5]: A significant increase in indenter modulus will be seen for many polymers as they age at thermal conditions.

However, these methods still have quite a few problems. Some need expensive testing equipment and dedicated testing procedures; some can only give vague data that cannot be interpreted properly, and most of them are destructive to the wire and cable themselves. More importantly, all the above methods cannot measure properties of interest *in situ*. Thus, it is highly desirable and imperative to develop a conve-
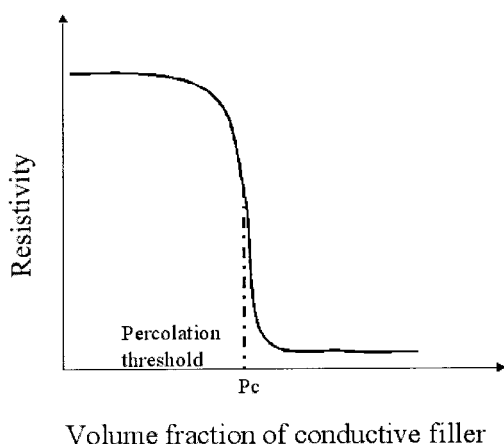
Figure 1 Percolation threshold of conductive polymer composites.

nient way for monitoring the aging condition of these cable materials. We have been attempting to develop an electrical approach to monitor the cable-aging condition.[6,7] The proposed method will develop an aging sensor that is embedded into the wire or cable insulation or jacket. With a simple *in situ* electrical measurement, the resistivity of the sensor correlates with aging-related degradation of material properties such as mechanical and physical properties. Thus, the measurement of the electrical property of the sensor can provide a practical solution to determine the remaining life of the insulation materials.

This new method is based on the percolation theory for conductive polymer composite (CPC) used as the sensor. The CPC materials consist of a random distribution of conducting filler dispersed in an insulating polymer matrix. For a semicrystalline polymer such as polyethylene, the conducting filler mainly exists in the amorphous phase of the polymer. Percolation theory has been used relatively successfully in modeling the general characteristics of resistivity of CPC materials. In brief, the percolation theory can be described as the conductivity of the CPC material that increases with the increase of volume fraction of the conductive particle, and a sharp change in conductance will happen when the volume fraction of the conductive particle reaches a critical value, the so-called percolation threshold (p_c), which is shown in Figure 1. The percolation threshold can be considered as the critical concentration of the conductive particle at which continuous conducting paths are formed. Experimentally, the percolation threshold can be determined from the dependence of the conductivity or resistivity of the CPC material on the conductive filler concentration.

CPC materials have been the focus of a number of studies on the theoretical aspects of their conductivity,[8] temperature sensitivity,[9] influence of additives on conductivity,[10–12] dielectric properties,[13] switching characteristics,[14] and influence of matrix properties.[15] However, there is not much research about the conductivity change of CPC for long-term applications, including those for *in situ*, nondestructive monitoring for wire and cable insulation materials at nuclear power plants. Produced by degradation of CPC materials, the volume percentage of the conductive particle will increase because of the loss of the volatile molecular weight part of polymer matrix, and thus, the conductivity of the composite increases. Because the initial conductive particle concentration of the CPC sensor materials is around the percolation threshold, the composite may show several orders of magnitude increase in conductivity because of the small increase of conductive particle volume fraction.

The aim of this work was to investigate the effect of thermal oxidation aging on the electrical behavior of conductive composite materials based on low-density polyethylene (LDPE) polymer matrix filled with carbon black at loading levels below the percolation threshold and to correlate the electrical properties change of conductive polymer composites with the changes of their physical properties. The knowledge will provide the basics about CPC sensor material characteristics for further development of cable-aging condition monitoring.

EXPERIMENTAL

Materials

Polyethylene is widely employed as the insulation material of wire and cable in nuclear power plants. A commercial grade of LDPE (Dow Plastics, USA) with a melt index of 2 g/10 min and a density of 0.921 g/cm^3 was used as the polymer matrix. The carbon black (CB) was Vulcan XC-72 (Black Pearls 2000, Cabot Corp., USA). The surface area and structure from adsorption number of dibutyl phthalate (DBP) for the carbon black are 143 m^2/g and 174 cm^3/100 g, respectively. The CB was incorporated into the base polymer by roll-milling method at a high temperature. Specimen tapes with a thickness of 0.3–0.35 mm were prepared by an extrusion process.

Oven aging

Oven aging of the composite materials was carried out at 180°C in an air-circulating convection oven (±1°C) equipped with thermocouples. Samples were taken out at intervals of specified aging time, and all the tests were performed after 24 h at room temperature.

Resistivity measurement

A DC voltage of 13.8 V was applied across the two ends of a specimen, and the current flowing through

TABLE 1
Materials Density Data

	LDPE	CB	LDPE/CB Calc[a]	LDPE/CB Expt[b]
Density (g/cm^3)	0.92	1.81	0.983	0.983

[a] Calculated from composite formulation.
[b] Experimentally determined by density measurement.

the specimen was measured with an autoranging picoammeter (Keithley 485). Then, the volume resistivity of the specimen was obtained via calculations with the geometric dimensions of the specimen. Each reported piece of data represents the average of measurements of at least three specimens.

Weight-loss measurement

For formulations subjected to aging test, separate specimens were prepared for weight measurement throughout the aging process.

Density measurement

Density of the specimens was measured by using the Archimedes approach,[16,17] where the sample is weighed in air and then in water by using a balance with a reproducibility of better than 10 μg. Each reported piece of data represents the average of measurements of at least three specimens.

Thermal properties measurement

The thermal behavior of the composites was characterized with a modulated differential scanning calorimeter (MDSC Model Q-1000, TA Instruments, USA). A sample of ~ 10 mg was sealed in a hermetic aluminum pan. Thermograms for samples were recorded from −80 to 250°C. The experiments were performed at a heating and cooling rate of 10°C/min under nitrogen atmosphere to avoid thermal degradation. The thermal stability of samples and the filler loading were investigated with a thermal gravimetric analyzer (TGA Model 2050, TA Instruments, USA). About a 20-mg sample was put into the TGA pan. A temperature scanning experiment was conducted with a ramping rate of 20°C/min from ambient temperature to 800°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

Sample composition

Many researchers have investigated the relationship between the room-temperature resistivity of the CPC materials with different CB contents. Based on the

results from ref.[18] and our data on percolation experiments,[7] we selected 13 wt % as the CB content for the initial LDPE/CB composite before aging. It was selected carefully so that the LDPE/CB composite is located just below the percolation and would demonstrate conductivity (or resistivity) changes of many orders of magnitude throughout the aging process. This will allow the LDPE/CB composites to better fulfill the electrical requirements as sensor materials for cable condition monitoring.[6] For thermal aging of polymer composites with antioxidants, some properties show no significant changes before the consumption of the antioxidants. However, the complete consumption of antioxidants will take a long time, even at accelerated aging conditions. To observe a relatively rapid aging process without waiting a long time, formulations without any antioxidant added were used in this study. The density of unaged composite, which is shown in Table I, was calculated from the material composition. Because the calculated density is equal to the experimental data, it is clear that the composite was ideally mixed.

Weight, density, and resistivity change versus aging time

The weights of the specimens were recorded during the aging process and the results are shown in Figure 2. The sample started losing weight remarkably after a few days' aging. Figure 3 shows the density measurement results. It can be seen that the density showed a persistent increase with aging time and leveled off by the end of the thermal aging.

Resistivity measurements were made on the samples aged at 180°C, with the results shown in Figure 4. Comparing these results to the density results in Figure 2, we note that the resistivity began to decrease dramatically after several days' aging, while the density increasing continuously. After spanning over about another 10 days, the resistivity decreased four
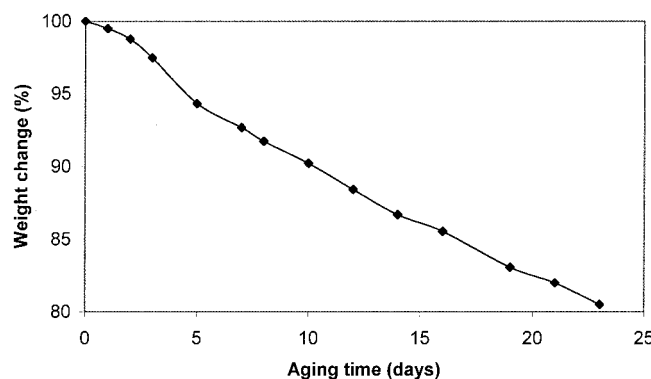

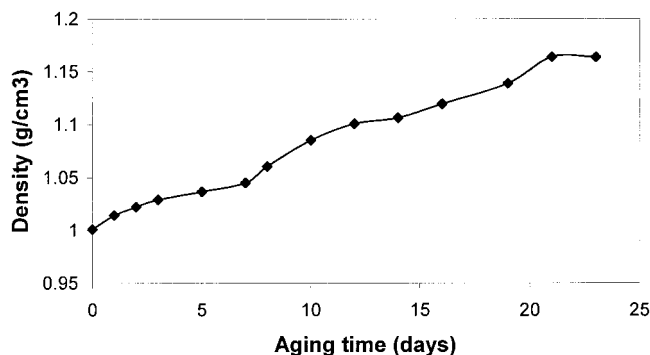**Figure 2** Weight change of LDPE/CB composite versus aging time.

Figure 3 Density of LDPE/CB composite versus aging time.

Figure 5 Correlation between resistivity, density, and CB volume fraction of LDPE/CB composite during thermal aging.

decades until becoming relatively stable toward the end of aging test, while the density increased nearly 10%.

To further understand the property changes of LDPE/CB composites during the thermal oxidation aging, detailed arguments about the density, filler volume, and resistivity changes of materials were conducted. There are some reasonable assumptions about the thermal oxidation aging process of composite materials, as follows: (1) the mixing of composite ingredients is ideal; (2) the thermal aging has no effect on CB fillers; (3) all of the changes in weight and density only come from the LDPE component.

Based on the assumptions and experimental data, CB volume fraction was calculated and plotted with density and resistivity of the composite in Figure 5. As can be seen from Figure 5, the density and resistivity have an opposite change trend against the CB volume fraction. Although the density changed almost linearly with CB volume, the resistivity decreased sharply after the CB volume reached a critical value, the so-called percolation threshold. In our case, this value is around 0.083 of CB volume fraction.

The results offer strong evidence that resistivity measurements of CPC materials could represent a po-
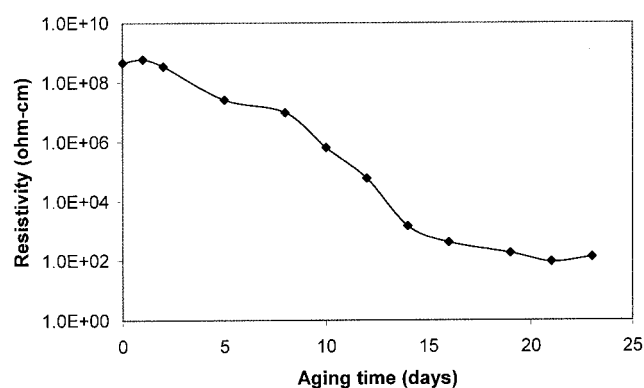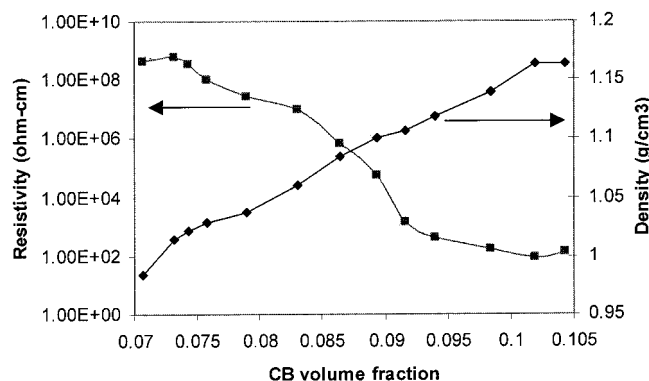
tential condition monitoring the aging of polymer materials. In comparison with existing density measurement, this electrical resistivity method has several advantages such as easy and inexpensive measurement, possible *in situ* setup, and nondestructive characterization. Above all, it is much more sensitive than the density method to the aging process. Due to the mechanism of density change during the polymer aging process, which will be discussed soon, the density change could not be as obvious as resistivity change. Density measurement has been used as an inexpensive approach to monitor the aging of polymer materials for a long time. Gillen et al.[3] have systematically investigated the density change versus aging time for the most important generic types of commercial nuclear power plant cable materials under thermal oxidation aging (or plus radiation aging) conditions. Table II partially shows their results. For these polymer materials, the highest change of density after aging was EPR, about 30% increasing; the lowest was only 1.1%, increasing for chlorinated polyethylene (CPE). Although these results were obtained from unfilled polymer, we can deduce the density change for filled polymer composites would not be very obvious either, because the density change of the composite materials during thermal aging mainly comes from the change of polymer matrix.

Thermal properties change versus aging time

The changes of the polymer matrix in composites during the thermal oxidation process were investigated by modulated DSC regarding its crystallinity. Figure 6 shows the DSC diagrams for LDPE/CB composite after aging at different times. It should be noted that the currently used aging temperature of 180°C was far above the crystalline melting point for LDPE. During the very initial experiment period, the sample recrystallization can happen to the ex-

Figure 4 Resistivity of LDPE/CB composite versus aging time.

TABLE II
Density Changes of Some Cable Materials at Thermal and Radiation Aging Condition[3]

Material	Initial density (g/cm^3)	End density (g/cm^3)
Chemically crosslinked polyethylene (XLPE)[a]	1.645	1.752
Chlorosulfonated polyethylene (CSPE)[a]	1.605	1.66
Chloroprene (CP)[b]	1.473	1.498
Ethylene-propylene rubber (EPR)[b]	1.31	1.69
Crosslinked polyolefin (XLPO)[b]	1.29	1.37
Proprietary (FR)[b]	1.27	1.345
Low-density polyethylene (LDPE)[a]	0.92	0.97
Poly (vinyl chloride) (PVC)[b]	1.37	1.45
Chlorinated polyethylene (CPE)[b]	1.375	1.39
Silicone (SI)[b]	1.305	1.34

[a] Aged at both thermal and radiation conditions.
[b] Aged at thermal only condition.

tent possible after being taken out from the oven and before any measurements of resistance and physical properties. As the experimental procedures were consistently followed throughout the aging process, the differences in the shape of the curves, the position of the melting peaks, and the heat of melting could well serve as the structural indicator of the polymer matrix (e.g., the distribution of the thickness, perfection of the lamellar crystals, and phase aggregation of LDPE polymer). As shown in Figure 6, the unaged LDPE/CB sample showed a high temperature of melting peak at 106.8°C, which corresponds to the T_m of the crystals consisting of polymer chain of high molecular weight and low degree of branching.[19] With increasing aging time, this melting peak appeared to move downward (e.g., to 87.6°C after 1 day aging, to 72.1°C after 5 days' aging), and it almost disappeared after 9 days' aging. This could be due to the chain scission reactions of the long molecular chains, which will promote chain branching and decrease the crystallization capability of the polymer matrix. Furthermore, the shoulder peak before the primary melting peak, which also became smaller and smaller with increasing aging time, could be attributed to less perfect crystal structures developed.
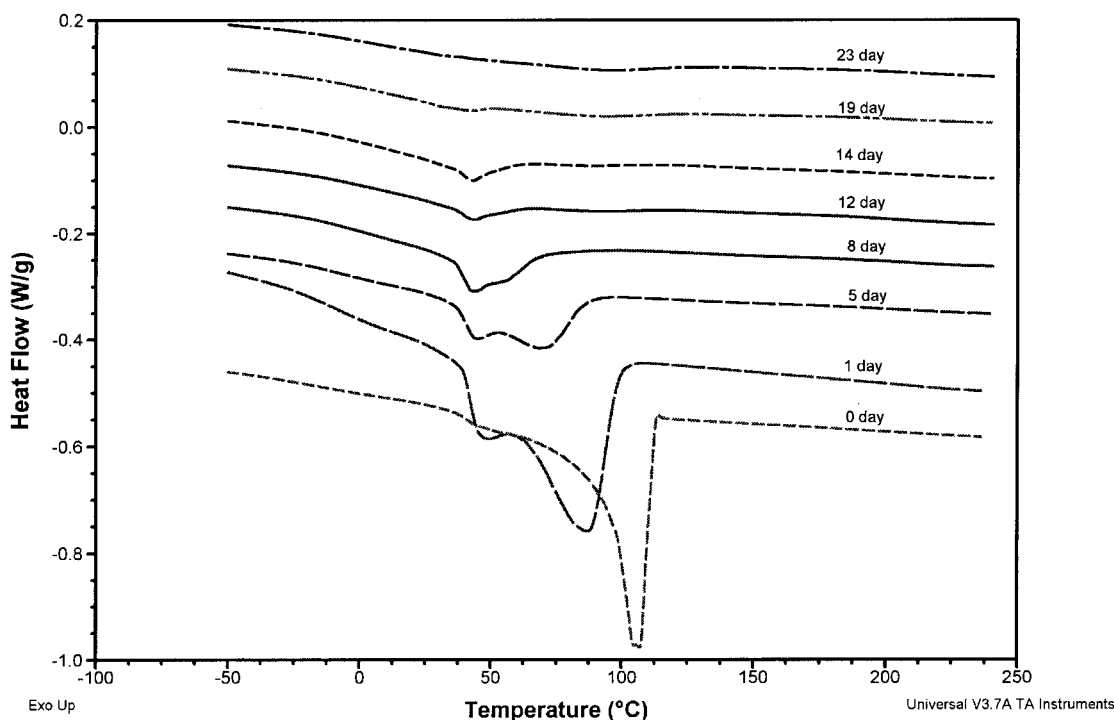

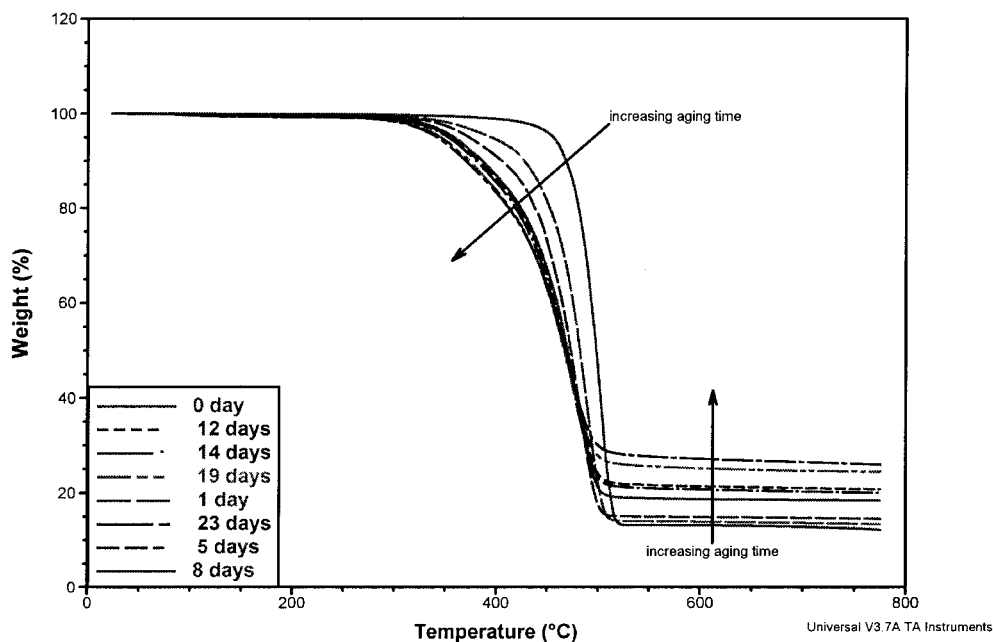**Figure 6** DSC diagrams of LDPE/CB composite versus aging time.

Figure 7 TGA diagrams of LDPE/CB composite versus aging time.

It is true that the chain scission reaction from thermal aging can produce low molecular weight chains; however, these broken chains could not fully recover crystallinity upon cooling. Therefore, the degree of crystallization in the polymer matrix was decreasing as the thermal oxidation aging proceeded. By the end of the thermal aging experiment, the crystallinity of the composites nearly disappeared, which indicates that recrystallization of polymer matrix simply cannot happen anymore. Thus, it can be seen that thermal aging would have a great influence on the polymer structure and morphology. Although CB is considered a medium-effect thermal antioxidant that can retard the thermal oxidation of polymeric materials,[20] it cannot prevent chain-scission reactions for LDPE matrix at a high-thermal aging temperature such as 180°C in our experiment. The degradation of the polymer matrix would result in broken molecules, traversing the crystalline regions, increasing the polydispersity of molecule, and disrupting the crystalline order.

Figure 7 shows the thermal stability of the composite with different aging times. As can be seen from the figure, the composite began to degrade from 300°C, and the polymer components almost burned out at 500°C. The plateau regions beyond 500°C of TGA curves represent the residue CB because the sample was burned under nitrogen atmosphere. It is obvious that both the carbon black concentration increased and the decomposition temperature of polymer decreased with increasing thermal aging time, which indicates the chain scission reaction of polymer chain and loss of low molecular weight components. This is consistent with the previous results on weight and density

measurements; the volume fraction of CB would increase while polymeric components were lost during the aging.

The degree of crystallinity of polymer matrix can be calculated by the equation

$$D = \frac{\Delta H_i / t_i}{\Delta H_i}$$

where ΔH_i is the heat of fusion of each sample (from DSC); ΔH_t is the heat of fusion of 100% crystalline LDPE (equal to 293.1 J/g, from ref. [19]); and t_i is the weight percentage of polymer component in each composite sample (from TGA).

The experimental data from DSC and TGA measurements are used for calculation of the degree of crystallinity of the polymer matrix, together with the CB content in the composite sample (see Table III). It is quite obvious that during the aging process, the composite sample kept losing polymer component, resulting in an increasing content of CB filler, while the crystallinity of the polymer matrix gradually deteriorated.

Discussion of material properties change during thermal oxidation aging

To understand the tremendous difference between the density and resistivity behaviors of CPC materials during thermal aging, one has to briefly examine the degradation mechanisms operative during the aging of polymers. When air is present during aging, oxidation usually dominates the degradation. The oxidation

TABLE III
Thermal Properties Data of Aged Samples

Aging time (day)	CB content (wt %)[a]	Polymer content (wt %)	Fusion heat of aged composite (J/g)[b]	Fusion heat of polymer (J/g)	Degree of crystallinity (%)
0	13.09	86.91	135.8	156.2	53.3
1	13.92	86.08	110.5	128.3	43.7
5	14.89	85.11	85.53	100.4	34.2
8	18.66	81.34	66.77	82.0	28.0
12	20.11	79.89	44.61	55.8	19.0
14	20.72	79.28	24.09	30.3	10.3
19	25.21	74.79	14.18	18.9	6.4
23	27.2	72.8	14.09	19.3	6.6

[a] From the residue value in TGA curve.
[b] From the integration area of melting peak in DSC curve.

mechanism typically leads to a mixture of crosslinking and scission processes, which generate both broken polymer chains with low molecular weight and oxidation products located along the polymer chain, as well as the gaseous degradation products. Previous research[21] has proved that these volatile products coming from the degradation of polyolefin included both oxygen-containing compounds such as carboxylic acids, ketones, hydrocarbons, lactones, and unoxidized hydrocarbons. In our work, the decrease in sample weight during thermal aging also indicated that chain scission was the predominate reaction for the LDPE/CB composite and the small molecular weight components were lost continuously.

Although our work showed that the crystalline region in polymer was decreasing in the thermal aging process, it had minor influence on the density compared to several other phenomena mentioned below, which can lead to density increases of composite materials. First, density increase comes from the replacement of hydrogen atoms along the chain with the much heavier oxygen atoms during oxidation. In addition, the crosslinking process induced by polymer degradation leads to shrinkage of the polymer network. Finally and most importantly, the mass loss of polymer component by thermal degradation will decrease the volume fraction of lower density polymer component and increase the relative weight fraction of the higher density fillers. These reasons can cause the increasing of material density.

Volume fraction of conductive filler is also crucial to the resistivity change of material. When it increases to the percolation threshold, the conductivity mechanism of CB in polymer composite would change from tunneling effect to direct contact,[22] and the resistivity of composite would decrease dramatically. This explanation applies to the resistivity change of the LDPE/CB composite as observed during the thermal oxidation aging. In addition to the volume fraction change of CB black, two other factors associated with the aging process may also affect the conductivity of

polymer composite, including polymer matrix chemistry and material structure and morphology. The random scission reactions in polymer degradation will produce molecules with unsaturated end groups and free radicals, smaller hydrocarbon chain molecules, or even the monomer molecules. These new oxygen-containing functional groups, such as carbonyl, hydroxyl group, may play an important role in the CB conductivity, typically enhancing its conductivity. On the other hand, with the degradation of the polymer matrix, the structure and morphology of the LDPE/CB composite will experience changes. The crystallinity of LDPE would deteriorate gradually and lose completely by the end of thermal aging. The CB particles, which were preferentially dispersed in the amorphous regions of LPDE polymer matrix, were separated by the crystalline regions before aging. After thermal aging, the disappearance of crystalline regions gave the CB particles more mobility in the polymer matrix and provided them more opportunities to contact each other.

In summary, the volume fraction change of conductive filler in LDPE/CB composites plays a key role in the change of density and resistivity as the composites experienced the thermal aging process. Unlike density, which only has a small increase after thermal aging, the electrical resistivity changes very sharply after the volume fraction of CB reaches the percolation threshold due to losses of polymeric components. So, the resistivity change can be used as a more sensitive parameter than density to monitor the aging process of conductive polymer composites.

Research efforts are being devoted to explore other polymer materials used for wire and cable in nuclear power plants (e.g., silicone, basically a rubber material in contrast to plastic polyethylene). The effects of thermal oxidation aging on the polymer matrix and the composite resistivity are being studied. Other aging factors, including irradiation, which are experienced by wire and cable materials at service, will also be investigated. A novel electrical condition monitoring

solution will be further developed based on these CPC sensor materials.

CONCLUSION

LDPE/CB conductive polymer composites were investigated as potential sensor materials for wire and cable condition monitoring in nuclear power plants. The resistivity of a CB (13 wt %) filled LDPE decreased dramatically during thermal oxidation aging. The change in resistivity upon aging spanned over four orders of magnitude, while the density of the composite only increased 10%. Thus, resistivity change of conductive polymer composites can be used to amplify the density change during thermal oxidation aging, as such could provide an *in situ* and nondestructive solution for aging monitoring purpose. The huge resistivity change of the LDPE/CB composite could be mainly attributed to the degradation of the polymer matrix with thermal oxidation aging and the resulting increase in volume fraction of the conductive CB filler. Thermal analysis of materials indicates polymer crystallinity deteriorated continuously and practically disappeared throughout the thermal oxidation aging.

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