

PTC Effect in HDPE Filled with Carbon Blacks Modified by Ni and Au Metallic Particles

Behzad Pourabbas,^{1,2} S. Jamal Peighambaroust²

¹Nanostructured Materials Research Center, Sahand University of Technology, Tabriz 51335-1996, Iran

²Polymeric Materials Research Center, Sahand University of Technology, Tabriz 51335-1996, Iran

Received 23 January 2006; accepted 21 November 2006

DOI 10.1002/app.26166

Published online 9 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Several types of positive temperature coefficient (PTC) composites are prepared by using Ni and Au modified carbon black. The major aim of this work was the lowering of the room temperature resistivity of the composites by enhancement of electrical conduction of the CB particles by incorporating metallic particles. Investigations showed that the metal particles fill the cavities and surface defects of the CB and thus surface free area reduces after modification. Metallic particles also change the nature of the CB particles after modification. Several types of PTC composites were prepared by using modified and unmodified CB by several loading level of filler. Measuring electrical properties of the PTC samples showed that the Ni modified CB reduce room temperature resistivity to lower than that of PTC composites prepared by unmodified CB. PTC

composites prepared by Au modified CBs showed very different properties compared to PTC composites prepared by Ni modified CB. Their resistivities were quite higher than the others showing a poor compatibility between the matrix and Au modified CB. The effect of thermal annealing also investigated on the electrical properties of the prepared composites. Room temperature resistivities reduced for most of the samples while PTC intensities increased after annealing. Theoretical bases are employed to discuss the room temperature resistivity and PTC behavior of the composites before and after annealing. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1031–1041, 2007

Key words: composites; polyethylene (PE); PTC; carbon black

INTRODUCTION

Conductive polymer composites made by incorporation of different volume fraction of conductive fillers like carbon black (CB), carbon fiber, and metal powder into a polymer matrix have found many applications such as electrostatic charge dissipation and electromagnetic interference shielding in the field of electronics and electrical industries. The conduction mechanism in CB-filled composites are investigated to be formation of a conduction network with electron tunneling or hopping rather than electron transfer through the contacted CB particles.¹ Positive temperature coefficient of resistance (PTC) composites are commonly employed in a wide range of uses, including in temperature sensors, protection circuitry, microswitches, flow meters, self-regulating heating elements, and self-resetting over current protection elements.² The main feature of the PTC effect is that with heating, system shows a sharp increase in resistivity around the melting point of the polymeric matrix, namely switching temperature (T_s). However,

above this region, a more conductive network may be formed, and a lower resistivity will be observed. This phenomenon is called a negative temperature coefficient (NTC) effect.³ The ratio of maximum resistivity to the room temperature resistivity is defined as PTC intensity.

A comprehensive theory describing the PTC/NTC phenomenon has not been completely established yet. However, PTC effect due to the interruption of conduction network near T_s and NTC effect by movement in molten polymer and formation of a new distribution of better uniformity and conductivity are widely accepted theories.⁴ Thermal volume expansion of the polymeric matrix is also investigated as one of the leading factors for PTC behavior.^{5,6} These PTC materials show poor reproducibility of resistivity during a long period of time or when undergoing thermal cycles.⁷ Studies have shown that the PTC behavior depends not only on the properties of CB such as particle size, aggregate shape, and dispersion state, but also on the characteristics of polymers such as chemical structure, crystallinity, and processing conditions.⁸ Dispersion of CB particles in composite is under control of dispersion forces and interfacial interaction between polymer and CB. Many researchers have tried to resolve the problem by surface modification of CB, oxidizing with nitric acid⁷ or pretreat-

Correspondence to: B. Pourabbas (pourabbas@sut.ac.ir).
Contract grant sponsor: Power Ministry of I.R. Iran.

ment of CB by titanate coupling agent,⁹ for example. So far, PTC composites are exclusively made by thermoplastic semicrystalline polymers such as polyethylene¹⁰ and Nylon.¹¹ However, thermoset polymers such as epoxy resin,¹² or even polymer blends^{6,13,14} have been employed. Radiation crosslinking of the polymeric matrix also have been used and investigated by several researchers.^{15–17}

Although, large number of investigations has already been done and many others are currently running, their subjects can be classified into some major headings: increasing PTC intensity, improvement of reproducibility, removing NTC effect, providing theoretical models and optimization of the processing condition. Increasing the PTC intensity can be achieved by two ways. Lowering the room temperature resistivity and/or increasing the resistivity at T_s . To lower the room temperature resistivity, one may use fillers in higher volume fractions. However, this method will be accompanied with rheological and processing problems. From the other hand, it will reduce the height of PTC peak in resistivity-temperature curve which means a reduced PTC intensity. Using substantially more conductive fillers such as metallic powders, would be the next way to lower the resistivity at room temperature. However, metallic powders generally suffer from the oxidation of the metallic particles and the corresponding deterioration of the electrical properties of the composite.¹⁸ From the other hand, and by the fact that the conductive fillers are added in 20–30 wt %, using chemically stable and precious metals, Au and Pt for example, obviously will increase the cost of the final product. Because of some reasons including better surface compatibility, chemically inertness and being accessible in different types in low cost, carbon black has been the widely used conductive filler in production of PTC composites. Several grades of CBs with different properties and electrical conductivity are available from different manufacturers. Although, different properties of CB are involved and must be taken into consideration in the preparation of CB filled polymers however, it is predictable that more conductive CBs with a good level of dispersion will endow PTC composites a lower electrical resistivity at room temperature. Surface modification of CB is a common process which takes place for several purposes and by several different methods.^{19–21} However, there was not any record available regarding to the increasing of electrical conductivity by any kind of surface or bulk modification of CB.

The present work is an attempt to modify CB with metallic particles and investigation of electrical properties and PTC effect in the prepared PTC composites. The modification has been carried out by Au and Ni metallic particles on CB and the selected matrix was high density polyethylene (HDPE).

EXPERIMENTAL

Materials

Carbon black used in this work was Printex-V supplied from Degussa, Germany and the used HDPE was EA6070 which purchased from Arak petrochemical company, Iran. CB particles were washed with toluene and were used after drying at 80°C for 24 h in an oven. $H(AuCl_4) \cdot 3H_2O$ and $NiCl_2 \cdot 6H_2O$ were the sources of gold and nickel respectively, both purchased from Merck, Germany, as high pure laboratory grade. Other chemicals used in this work were mostly purchased from Fluka and Merck chemical companies and were used as received unless otherwise mentioned in the procedures.

Instruments

A single beam UV–Visible spectrophotometer Milton Roy 402 was used for quantitative measurements of concentrations. Electrical resistivity of the PTC samples was measured by using a digital multimeter (Keader[®] LDM-852A) or a LCR-meter (Escort[®] ELC-13C-131D) when the resistivity was lower than $10^7 \Omega$. For amounts higher than this value, a megger (Kyoritsu-3125) was used. A twin-roll mill was used to prepare the composites at 160°C with rolls rotating at 25 rpm. Porosity measurements were carried out by using Pascal 440 mercury porosimeter and Cambridge S360 Scanning Electron Microscope was used for electron microscopy studies.

Preparation of Ni modified CB particles

Surface modification of CB with dimethylglyoxime

To 500 mL 1% (w/w) ethanolic DMG solution in a beaker which was placed in a thermostatic 30°C water bath, 10 g of CB was added. After 0.5 h mixing, it was filtered, washed first with ethanol and then with water thoroughly and dried at 60°C for 24 h. This product is coded as CB-DMG in Table I and through out the text.

Adsorption of Ni^{2+} ions by CB-DMG

To 500 mL Ni^{2+} solution, 5 g of CB-DMG was added. The Ni solution was prepared by dissolution of appropriate amounts of $NiCl_2 \cdot 6H_2O$ in distilled water to reach a total concentration of 150 ppm with respect to Ni^{2+} . The pH of the solution was adjusted in 10 by adding droplets of diluted ammonia solution. The solution was mixed for 1 h by using a mechanical stirrer. During this time, the solution was continuously checked for Ni^{2+} concentrations. Small portions of the solution (~ 7 mL) were removed between periods of 5 min and after the CB particles

TABLE I
Encoding Table of the Materials Prepared or Used in This Work

Code	Description
CB or PC	Pure form of carbon black without any treatment or modification
TC	Carbon black which is washed with toluene
CB-DMG	Carbon black pre-treated with DMG
CB-DMG-X-Ni ²⁺	CB-DMG after adsorption of Ni ²⁺ ions from a solution containing X ppm of the ion
CB-X-Ni	Carbon black modified with Ni particles, X represent the Ni ²⁺ concentration (ppm) in the solution which was used in the adsorption stage of the ions by CB
CB-X-Au	Carbon black modified with Au particles; X represents the Au ³⁺ concentration (ppm) in the solution that was used in the adsorption stage of the ions by CB
PTC-PC-X %	PTC composites which are prepared by pure carbon black; X represents the weight percent of the filler in the composite
PTC-TC-X %	PTC composites which are prepared by toluene washed carbon black; X represents the weight percent of the filler in the composite
PTC-X-Ni-Y %	PTC composites which are prepared by Ni modified carbon black; X and Y represents the Ni ²⁺ concentration (ppm) in the solution which was used in the adsorption stage of the ions by CB and the weight percent of the filler in the composite, respectively
PTC-X-Au-Y %	PTC composites which are prepared by Au modified carbon black; X and Y represents the Au ³⁺ concentration (ppm) in the solution which was used in the adsorption stage of the ions by CB and the weight percent of the filler in the composite, respectively

were filtered off, the Ni²⁺ concentration was determined in the filtrate. The procedure was the standard spectrophotometric method²² at wavelength of 445 nm. At the end of mixing time, the product was collected on a filter paper and washed with water until complete removal of Ni²⁺ ions. This was being checked by using an ammoniacal DMG solution. It was then dried in an oven at 110°C for 24 h.

To prepare Ni modified CB with different amounts of adsorbed Ni, the procedure was repeated by 200, 250, and 300 ppm solution of Ni²⁺. These products are coded as CB-DMG-X-Ni²⁺ in this text while X denotes to the concentration of Ni²⁺ in the used solutions (Table I).

Reduction of adsorbed Ni²⁺ ions into metallic Ni particles

Under a fume cupboard, 25 mL 5% (w/w) solution of NaBH₄ in water was added to 250 mL water containing 1 g CB-DMG-X-Ni²⁺ drop by drop. The solution was being mixed by a magnetic stirrer. After 0.5 h mixing, the product was filtered, washed completely with water and was dried at 110°C for 24 h in an oven. These products are coded as CB-X-Ni in the text while X represents the concentration of the Ni²⁺ solutions used in the previous stage (Table I).

Preparation of Au modified CB particles

Adsorption of Au³⁺ ions onto CB particles

To 250 mL Au³⁺ solution, 5 g of CB was added. The Au solution was prepared by dissolution of appropriate amounts of H(AuCl₄).3H₂O in distilled water to reach a total concentration of 150 ppm with respect to Au³⁺. The solution was mixed for 1 h by

using a mechanical stirrer. During this time, the solution was being checked continuously for Au³⁺ concentrations. Small portions of the mixture (~ 7 mL) were removed between periods of 5 min and after the CB particles were filtered off, the Au³⁺ concentration was determined in the filtrate. The used analytical method for the measurement of Au³⁺ concentration was a conventional iodometric titration.²³ At the end of mixing time, the product was filtered and washed with water. It was then dried in an oven at 110°C for 24 h. To prepare CB particles with different amount of Au, the procedure was repeated with 200 and 250 ppm of Au³⁺ solutions. These products are coded as CB-X-Au³⁺ through out text which X denotes the concentration of Au³⁺ ions in the used solutions (Table I).

Reduction of adsorbed Au³⁺ ions into metallic Au particles

Under a fume cupboard, 25 mL, 5% (w/w) solution of NaBH₄ in water was added to 250 mL water containing 1 g CB-X-Au³⁺ drop by drop. The solution was being mixed by a magnetic stirrer. After 0.5 h mixing, the product was filtered, washed completely with water and was dried at 110°C for 24 h in an oven. These products are coded as CB-X-Au in the text which X represents the concentration of the Au³⁺ solutions used in the previous stage (Table I).

Preparation of the PTC composites

The composites were prepared by mixing the modified an unmodified CBs with HDPE. The mixing was performed in a twin-roll mill at 150°C, during 30 min mixing time with average rolls rotating speed of 25 rpm. Several types of PTC composites were

prepared by using different loading levels of CB, ranging from 20 to 35% (w/w, filler/matrix). These products are coded as PTC-X-Ni-Y or PTC-X-Au-Y in the text. In this coding system, X and Y denotes to the concentration of the related ion (Ni or Au) in the solutions used in the ion adsorption stage and loading level of the CB in the prepared composites, respectively, (Table I). After removal of the product, it was cut into small pieces for the next compression molding stage.

Preparation of PTC test samples

After preparation of the composites, they were compression molded into 0.7 mm thickness sheets. The sheets were cut later as 1×1 cm squares. To electrical measurements become possible, they were placed between two nickel foils (0.15 mm thickness each). Therefore, total thickness of each sample was 1 mm. For the nickel foils remain attached during the examination, the whole sample was being supported by an especial coverage known as thermal varnish. Thermal varnish is a flexible rubber-like tube which undergoes large extent of shrinkage upon heating. Therefore, when the test sample was placed inside the varnish tube and after shrinkage, the varnish coverage holds the sandwiched PTC composite and nickel foils tightly together. Two copper wires were soldered on the surfaces of the nickel electrodes through the holes established on the varnish layer. To remove all mechanical and thermal stresses, electrical resistivity of the samples in different temperatures was measured after 48 h relaxation. Measurements were carried out on-line while the test samples were immersed in a silicon oil bath with a temperature increasing rate of $3^\circ\text{C}/\text{min}$. The measured electrical resistivities were converted into specific resistivity (ρ) by using simple geometric calculations.

RESULTS AND DISCUSSION

Modification of CB with metallic particles

Modification of CB with Ni metallic particles

Carbon black in addition to its electrical conductivity is mostly known as a powerful absorber because of its surface characteristics and ability to adsorb many other compounds. This is one of the reasons for its wide range of applications in several different industries since several years ago. It was enough to authors to suppose that CB will adsorb Ni^{2+} ions from solution. If it happened, it would be easy to modify CB with Ni metallic particles after the adsorption of the ions and a subsequent reduction of ions into metallic state. Unfortunately, our initial examinations showed clearly that the Ni^{2+} ions can not be adsorbed by CB. Tracing the Ni^{2+} ions concen-

tration in an aqueous solution which was being in contact with CB showed that no any amount of the ions were adsorbed even after 2 h stirring. The reason might be due to the nonpolar characteristics of the CB surface. By the other words, it can not be soaked by aqueous polar ionic solution which is a requirement to adsorption happen. Due to the fact that CB surface is more compatible with organic molecules, a surface premodification has been performed on its surface by using dimethylglyoxime (DMG). DMG is a known classical molecule which makes strong complexes with Ni^{2+} . Therefore, DMG modified CB samples were prepared by mixing CB in an ethanolic 1% (w/w) DMG solution. The DMG pretreated CB, adsorbed Ni^{2+} ions completely and easily from an aqueous solution of the ions, in a pH controlled at 10. Ni^{2+} concentration measurements in the solution showed that they were adsorbed completely after 0.5 h mixing. Metallic Ni particles finally produced on the CB surface after a reduction reaction which was carried out by 5% aqueous solution of NaBH_4 . Figure 1 shows the SEM photographs for bare CB, CB-DMG, CB-DMG- Ni^{2+} , and CB-200-Ni. As shown in Figure 1, after pretreatment the surface cavities are covered by DMG. However, DMG has been removed from the surface at the end of process likely due to the reduction reaction of NaBH_4 with DMG [Fig. 1(d)]. Comparison of SEM micrographs for CB with that of CB-200-Ni [Fig. 1(a,d)] reveals the Ni metallic particles have placed in the cavities and surface defects of the CB aggregates. Using mercury porosity measurements it was obtained that the surface free area reduces from 171 to 99 m^2/g after modification with Ni (CB-200-Ni). Changing surface characteristic after modification is the key factor effective on the electrical properties of the PTC samples which will be discussed later in this section.

Modification of CB with Au metallic particles

In contrast to Ni^{2+} , CB adsorbs Au^{3+} ions easily even from an aqueous solution. The reason for this different behavior for Au^{3+} versus Ni^{2+} may be due to the sulfur containing molecules which exist substantially on the surface of CB. The complex formation between these and Au^{3+} ions, leads to adsorption of gold ions from the solution. After adsorption of gold ions, they were reduced into metallic particles by aqueous 5% NaBH_4 solution. Figure 2 shows the SEM photograph for CB-200-Au after modification. As it can be seen and also discussed for the case of modification with nickel, surface cavities have been filled by metallic Au. In this case, the surface area is reduced to 56 m^2/g based on results obtained after examination with mercury porosity measurements.

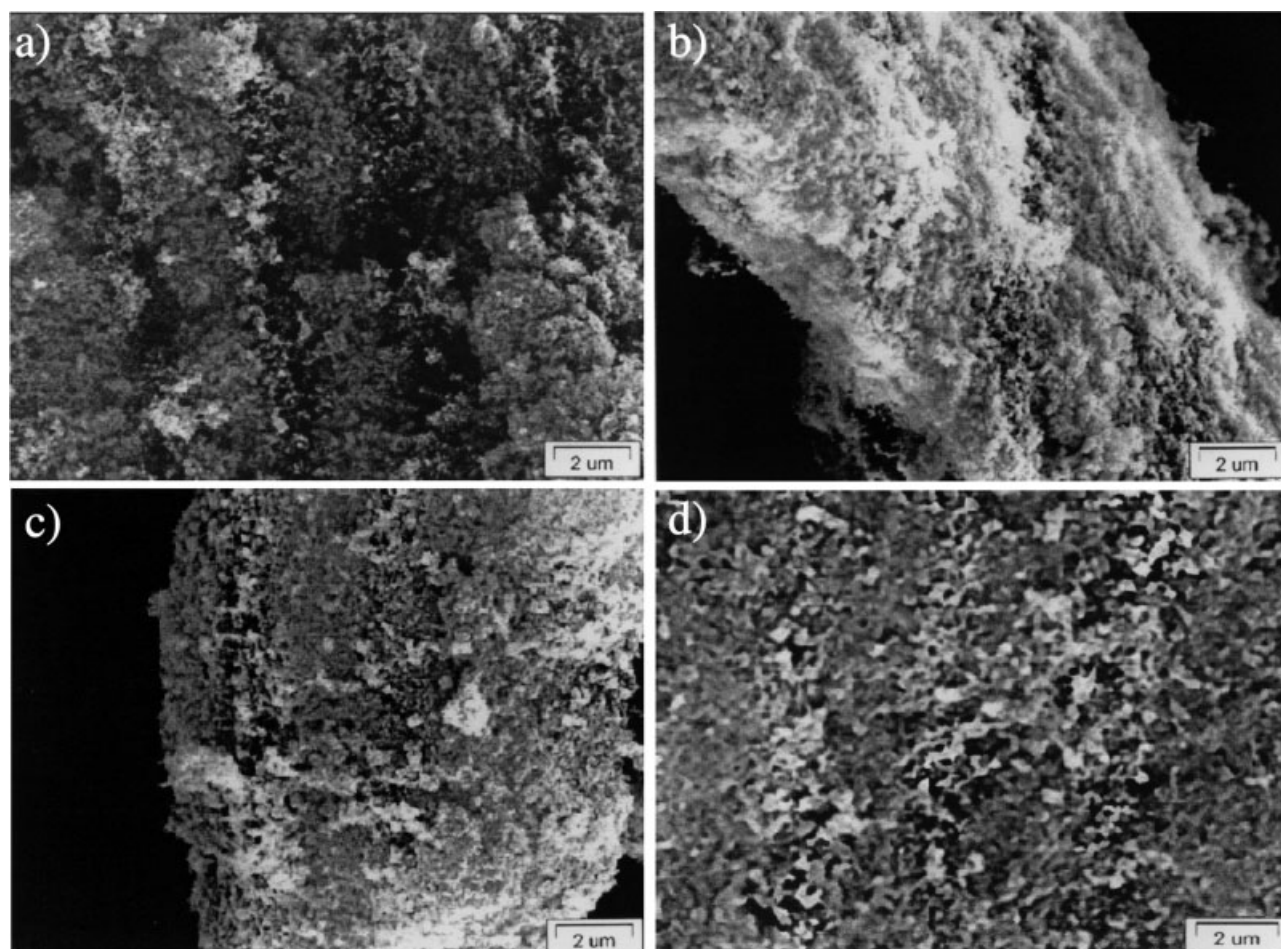


Figure 1 SEM photographs for (a) pure CB, (b) CB-DMG-200-Ni²⁺, (c) CB-DMG-Ni²⁺, and (d) CB-200-Ni.

Electrical properties of the PTC composites

Room temperature electrical resistivity

In this work PTC samples were prepared by filler loading level of 20, 25, 30, and 35% by weight. The percolation thresholds for most of the PTC samples were determined to be around 30% of filler content. Figure 3 shows the room temperature specific resistivity (ρ_{RT}) for PTC samples in their upper percolation region. Figure 3 contains the most important results which are being discussed in the following sections. Firstly, the resistivity is lower for each of the members in 35% series compared to their corresponding members in 30% series. The reason is clear. Electrical resistivity of the filled PTC composites is dependent on the loading level of the conductive filler. The second result which can be obtained directly from Figure 3 is that the room temperature resistivity is higher for PTC samples prepared by toluene washed CBs in respect to they which are prepared by pure CB. The difference is obviously larger for 30% level of filler loading. It has been obtained and reported by previous workers that room temperature resistivity of PTC composites increases upon pre-

treatment of CB, oxidizing with hot HNO₃ for example.² It is attributed to the production of some certain chemical groups which arrest electrons and thus increase the electrical resistivity of the CB particles.²



Figure 2 SEM photograph for CB after modification with Au metallic particles.

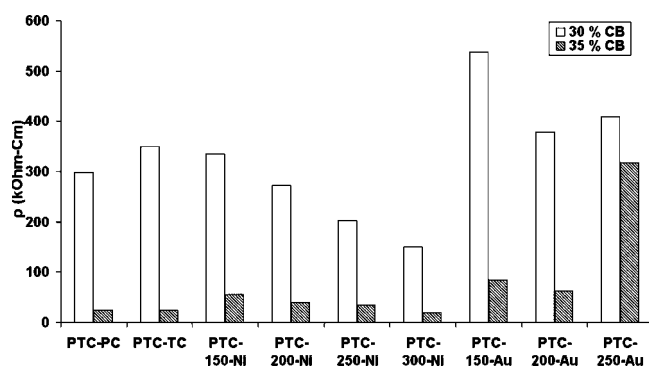


Figure 3 Room temperature specific resistivity (ρ_{RT}) for PTC samples in their upper percolation region.

In our results obtained for toluene washed CBs the same situation is also involved. Adsorption of toluene molecules leads to formation of a shielding layer which prevents electron hopping in the conduction network and thus increases the resistivity. Further, existence of toluene molecules changes the surface characteristics of the CB particles and aggregates which in turn, results in a different filler-polymer interaction and dispersion condition of the particles in the composite. At higher contents of filler, 35% for example, the deficiency is overcome by the larger number of the conductive particles in the conduction network and the room temperature resistivity reaches to an equal value for PTC-TC-30% and PTC-TC-35%.

The next result in Figure 3 is about the effect of modification of CB on ρ_{RT} . In 30% series, ρ_{RT} increases initially and decreases later by increasing the metallic Ni content in CB. In other words, the resistivity increases from PTC-PC-30% to PTC-TC-30% and reaches to a maximum at PTC-150-Ni-30%. However, decreases gradually later with increasing the metal content in CB. In this way PTC-300-Ni-30% has the lowest resistivity in series. Room temperature resistivity and PTC effect has been studied previously for PTC composites filled with metal particles like Ni powder. According to the work, metal filled PTC composites had shown a reduced resistivity versus those which were filled with normal kinds of CB.⁸ It is also shown that the resistivity also decreases further by increasing the filler content.²⁴ This must be noted that these phenomena are observed when the metal fillers were used in the pure form and higher weight percentages, 40% for example.⁸ In our results, the initial increasing of the resistivity which is observed for the modified CBs can be interpreted in terms of the surface characteristics change. As discussed earlier, Figure 1 and results from porosimetry measurements revealed that the metallic particles fill the surface cavities and reduce the total free surface area of the CB after modification. From the other hand, after modification with metal particles, the sur-

face properties and nature of the CB changes in some extent which depends on the amount of the surface metallic particles. This will lead to a weak polymer-filler interaction and less-efficient conduction network. This can be considered as the predominant factor for increased room temperature resistivity of PTC-150-Ni-30%. On moving to the next members in the series, the resistivity decreases as the metal content increases. In this case the dominating factor is obviously the increasing of the substantial electrical conductivity of the particles which is occurred in effect of modification. Samples PTC-200-Ni-30%, PTC-250-Ni-30% and PTC-300-Ni-30% have ρ_{RT} values lower than that of PTC-PC-30% and PTC-TC-30%. The same discipline is also observed for the 35% series in Figure 3. In this case ρ_{RT} also decreases by increasing the metal content, from PTC-150-Ni-35% to PTC-300-Ni-35% monotonically and the same discussion is applied as for the case of 30% series. In the series, PTC-300-Ni-35% is the only sample which its ρ_{RT} is lower than that of PTC-PC-35%.

The situation is different for PTC samples prepared by Au modified CBs. As it can be seen in Figure 3, ρ_{RT} values for these samples are quite higher in comparison with the other samples. Although Au filled PTC composites have not been studied in the literature however, organic/metal interface effect in some electrical application was found to be subject of some scientific works.^{25,26} It is revealed that there is an imperfect adhesion between organic compounds to the Au metallic surface. This produces molecular-sized blind alleys (structural trap) which finally trigger the tunneling injection of electrons from the Au surface. Therefore and due to the lack of perfect contact, admixture of Au and organic polymeric matrices can not build up a suitable electrical contact which in PTC composites leads to higher room temperature resistance.

Another interesting result, which can be obtained from Figure 3, is that ρ_{RT} in PTC-150-Au-30% and PTC-150-Au-35% decreases initially in PTC-200-Au-30% and PTC-200-Au-35%, but increases again for samples PTC-250-Au-30% and PTC-250-Au-35%. It is a very complex behavior and can not be discussed without further experimental data and therefore, the problem will remain open until future works. However, appearance of a minimum amount for ρ_{RT} in these series shows the incorporating of two factors acting in opposite directions by increasing the Au content in CB. One is certainly the increasing of inherent electrical conduction of the particles with increasing Au content. This is the same argument which was applied for decreasing ρ_{RT} with increasing Ni content in the Ni series. The second and opposing factor is probably in relation to the increasing of the Au/polymer interface by increasing the Au content in the modified CB.

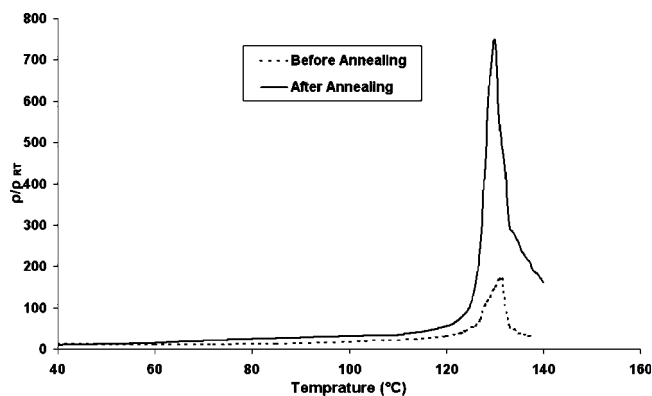


Figure 4 The variation of resistivity with temperature for sample PTC-300-Ni-35%, before and after annealing.

PTC intensities

Figure 4 is a plot of specific resistivity ρ variation with temperature for sample PTC-300-Ni-35% showing the PTC peak with subsequent NTC effect.

The PTC intensities i_{PTC} and other electrical properties including ρ_{RT} , maximum specific resistivity at T_s ρ_{max} and switching temperature T_s are collected in Table II for the prepared PTC composites. As is shown in Table II, i_{PTC} values are spread over a range of numerical values from 0.769 to 5.141. PTC-PC-30% has the minimum amount while the maximum is for PTC-200-Au-35%. Beside these minimum and maximum, other samples have shown a moderate values for i_{PTC} ranging from 1.3 to 3.3. Other PTC samples prepared by pure CB and toluene

washed CB show a similar value centered at 1.8. Many of samples with i_{PTC} values greater than 2 also are observed in Table II. It is an interesting result that the highest i_{PTC} values in Table II are obtained for PTC samples prepared by modified CBs. According to the works carried out on the theoretical aspects of PTC behavior several mechanisms and models have been proposed. Some authors believe in the widening of the gaps between conducting particles happening at T_s .²⁷

Other authors attributed the behavior to the decrease of the filler volume fraction due to the overall thermal expansion of the conducting system around T_s .^{28–30} Deagglomeration or breakage of the conducting network has also been proposed by several other authors for the PTC phenomenon.³¹ Hindermann-Bischoff and Ehrburger-Dolle³² have investigated the PTC phenomenon by using experimental evidences collected from analyzing the DC and AC conductivity and influences on the thermal expansion of the matrix in a series of CB filled polyethylene composites. They have concluded that in semi-crystalline polymeric metrics the relative amount of amorphous and crystalline regions also depend on the morphology and on the volume fraction of CB. They have also pointed out the importance of interpenetrating of CB aggregate on the electrical behavior of the composites and which is modified during the matrix melting induced PTC effect. This is characteristics of CB aggregates which are able to interpenetrate each others because of their fractal properties.

TABLE II
Electrical Properties of the Prepared PTC Composites

Sample	i_{PTC}^a	ρ_{RT}^b ($\times 10^3 \Omega \text{ cm}$)	ρ_{max}^c ($\times 10^6 \Omega \text{ cm}$)	T_s^d ($^{\circ}\text{C}$)
PTC-PC-30%	0.769	298.4	1.7	127
PTC-PC-35%	1.882	24.2	1.8	129
PTC-TC-30%	1.852	349.3	24.8	129
PTC-TC-35%	1.850	24.3	1.7	130
PTC-150-Ni-30%	1.742	334.7	18.5	131
PTC-150-Ni-35%	1.331	55.5	1.2	130
PTC-200-Ni-30%	1.31	272.9	5.6	129
PTC-200-Ni-35%	2.185	39.3	6.0	127
PTC-250-Ni-30%	1.096	202.1	2.5	131
PTC-250-Ni-35%	1.631	35.6	1.5	129
PTC-300-Ni-30%	3.281	149.7	285.7	129
PTC-300-Ni-35%	2.28	19.5	3.3	131
PTC-150-Au-30%	1.06	538.0	6.2	130
PTC-150-Au-35%	1.991	83.8	8.2	129
PTC-200-Au-30%	3.05	379.1	432.7	129
PTC-200-Au-35%	5.141	62.0	8585.0	126
PTC-250-Au-30%	2.41	409.1	106.3	130
PTC-250-Au-35%	2.945	318.0	280.5	131

^a PTC intensity, defined as logarithm ratio of ρ_{max} to ρ_{RT} .

^b Specific resistivity at room temperature.

^c Specific resistivity at T_s .

^d Switching temperature.

TABLE III
Electrical Properties of the Prepared PTC Composites After Thermal Annealing

Sample	i_{PTC}^a	ρ_{RT}^b ($\times 10^3 \Omega \text{ cm}$)	ρ_{max}^c ($\times 10^6 \Omega \text{ cm}$)	T_s^d ($^\circ\text{C}$)
PTC-PC-30%	3.668	26.7	124.1	131
PTC-PC-35%	2.766	20.0	11.6	130
PTC-TC-30%	2.292	36.3	7.1	132
PTC-TC-35%	2.496	17.8	5.6	132
PTC-150-Ni-30%	2.825	236.6	158.0	129
PTC-150-Ni-35%	3.716	54.1	281.4	131
PTC-200-Ni-30%	2.86	212.9	157.7	130
PTC-200-Ni-35%	3.854	32.9	234.7	132
PTC-250-Ni-30%	2.6	187.1	78.8	130
PTC-250-Ni-35%	3.540	29.7	103.1	131
PTC-300-Ni-30%	3.072	164.7	194.4	131
PTC-300-Ni-35%	2.872	21.8	16.3	130
PTC-150-Au-30%	2.8	445.7	105.0	131
PTC-150-Au-35%	2.533	386.1	132.0	130
PTC-200-Au-30%	3.17	388.6	576.9	130
PTC-200-Au-35%	4.575	246.7	9271.4	127
PTC-250-Au-30%	2.76	326.1	187.4	131
PTC-250-Au-35%	3.001	211.3	211.8	131

^a PTC intensity, defined as logarithm ratio of ρ_{max} to ρ_{RT} .

^b Specific resistivity at room temperature.

^c Specific resistivity at T_s .

^d Switching temperature.

Therefore, by taking all the theories mentioned above into account, the reason for variation of i_{PTC} between PTC samples prepared by different modified and unmodified CBs in this work can be attributed to the characteristics of CB. Because of the fact that modification changes the surface properties of the CB aggregates, aggregate properties and relative amount of crystalline and amorphous regions in the matrix changes upon modification, and finally affect the i_{PTC} .

Effect of thermal annealing on PTC intensities and NTC behavior

In the preceding section, those properties of the PTC samples were being discussed which were obtained for PTC samples before applying any thermal treatment or annealing. It has been shown that thermal treatments can improve electrical properties of PTC composites. The variation of resistivity with temperature is shown in Figure 4 before and after annealing for the sample PTC-300-Ni-35%. Y.H.Hou et.al. has investigated the effect of postheat treatments on ρ_{RT} and i_{PTC} in crosslinked and uncross-linked series of PTC composites.¹⁷ They have concluded that annealing is necessary for crosslinked PTC materials. Moreover, under optimized annealing condition, electrical networks of improved quality coupled with low ρ_{RT} and high i_{PTC} can be obtained according to their results. In uncross-linked composites, redistribution of CB in response to the variation in the matrix morphology is determined as the predominant mechanism for improved electrical properties. In this work, and to investigate the effect of thermal annealing on

the electrical properties, thermal annealing were applied on the prepared PTC composites at 100 $^\circ\text{C}$ for 24 h and electrical measurements carried out after 24 h relaxation time. Table III shows the results. As can be seen, after thermal annealing all the electrical properties in Table III are changed compared to Table II. Values of ρ_{RT} are compared before and after annealing for 35% series of the composites in Figure 5. In general, room temperature resistivity is reduced for PTC samples prepared by pure CB, toluene washed CB and Ni modified CBs. The effect is more pronounced for PTC-CB-30% and PTC-TC-30%. For the PTC series prepared by Au modified CBs a different and complex effect is observed so that ρ_{RT} is increased for PTC-200-Au-30%, PTC-150-Au-35% and PTC-200-Au-35% after annealing as is shown in Figure 5 and data provided in Table III.

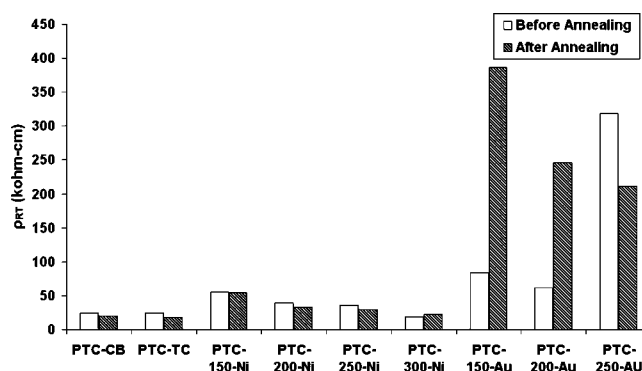


Figure 5 The effect of annealing on ρ_{RT} for the composites containing 35% of the filler.

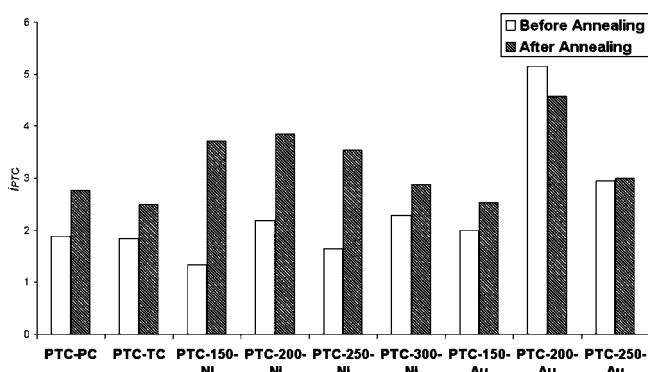


Figure 6 The effect of annealing on i_{PTC} for the composites containing 35% of the filler.

According to the results obtained by previous workers, there is not any general rule for increasing or decreasing of ρ_{RT} in PTC materials after heat treatment. Improvements of crystallinity and crystalline perfection as well as uniformization of the crystallite dimension are mentioned as the factors leading to decrease in ρ_{RT} after annealing.¹⁷ It is also believed that if reagglomeration of the fillers happens, a new conduction path which is heterogeneous in structure and less effective in conduction will form and ρ_{RT} increases consequently.¹⁷ In Figure 6, i_{PTC} values are compared for the same series in Figure 5. It can be seen that for almost all of the samples i_{PTC} is increased after annealing. The same results are also obtained for PTC materials by other workers.^{17,33}

It is mentioned that behavior of melting, crystallization and aggregate "large size" properties of the matrix as well as long spacing and lamellar size affect the PTC intensity after annealing.³³ In general, i_{PTC} and its increase upon thermal annealing is a phenomenon that depends on the property changes of the matrix during the annealing process. However, ρ_{RT} and its variation upon annealing is a quite complex behavior, which depends on any kind of factors capable to influence the quality of the conduction network including matrix thermal response and changes in properties of the conducting filler. In Table III, T_s s are also changed and mainly increased compared to Table II. It gives a support for the above discussion that crystalline structure of the matrix changes during the annealing process.

The electrical properties and the PTC effect were also checked for thermal cycling between room temperature and 140°C (above the T_s). This behavior has an importance from practical point of view for PTC resistors. They must remain effective after several thermal cycles, which might occur during service time. Figures 7 and 8 show the influence of thermal cycling for the after-annealed samples of PTC-250-Ni-35% and PTC-250-Au-35% respectively. The samples were heated by 3°C/min heating rate and then allowed to

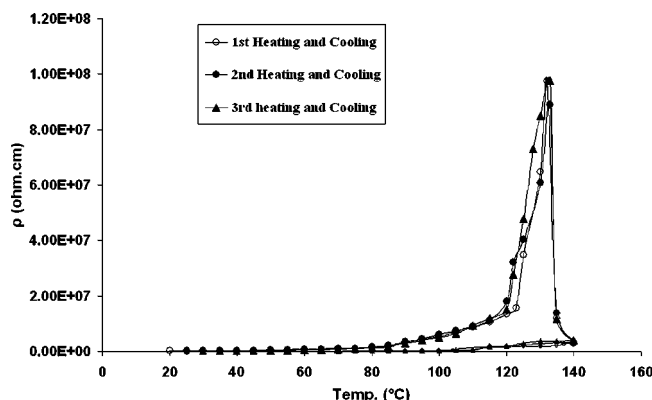


Figure 7 The electrical behavior of the after-annealed sample of PTC-Ni-250-35% in thermal cycling between room temperature and 140°C.

cool by normal cooling rate, that is, without applying any cooling devices. Three cycling were applied.

As is seen, they have shown the PTC peak at their premeasured T_s temperature ($\sim 130^\circ\text{C}$). However, upon cooling, the resistivities were decreasing by temperature reduction gradually without passing over the PTC peak again. The adoption of the repeated cycles is acceptable in experimental range of errors. The best reproducibility is usually observed in crosslinked (induced by radiation or chemical agents) PTC composites.^{15,16} This is reported to be due to the fixed conduction network which remain unchanged during the thermal cycling. In other words, cross-linked network prevents the conduction network from reconstruction while the temperature is above the T_s . This also diminishes or removes the NTC effect with the crosslinked samples. However, the reproducibility observed in Figures 7 and 8 is interesting and must be due to another reason because, they are for annealed but uncross-linked samples. There are records available in literature dealing with the annealing effect on the electrical properties of the

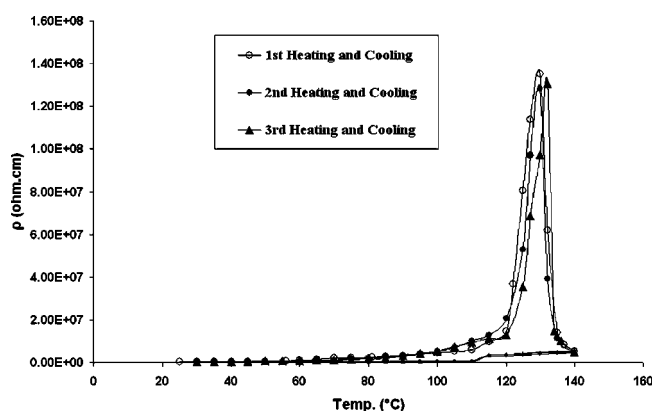


Figure 8 The electrical behavior of the after-annealed sample of PTC-Au-250-35% in thermal cycling between room temperature and 140°C.

crosslinked and uncross-linked PTC composites however, without any discussion on the reproducibility of the ρ - T behavior for uncross-linked PTC composites.^{4,17} To the authors' opinion, the observed reproducibility observed in our samples must be due to the applied experimental conditions. The cooling rate was too slow because the samples were still on the hot oil-bath when cooling. This provide enough time to matrix to reach to a reproducible crystalline state in each thermal cycle as it had in the first cycle. It is certainly known and has been reported that the ρ - T behavior depends on the crystallization history of the composite. However, this must be investigated exactly by future researches.³⁴

CONCLUSIONS

Based on the above discussions, the following statements can be made:

- a. CB can be modified by metallic particles such as Ni and Au. Although CB can not adsorb Ni²⁺ ions directly from an aqueous solution however, it can be done by using an indirect process including a premodification of CB particles with DMG and then, adsorption of Ni²⁺ ions and later reduction of the ions into metallic state.
- b. In contrast to Ni²⁺, CB adsorbs Au³⁺ ions easily from an aqueous solution. Subsequent reduction of the ions into metallic state will produce metallic particle on the surface of CB.
- c. After modification of CB with metallic particles, the particles fill the surface cavities of the CB leading to decrease in free surface area. Not only the free surface area reduces, but also the nature of the surface changes due to the existence of metallic particles in the surface of the CB aggregates.
- d. Reduction of free surface area as well as changes in surface properties of the CB influences the matrix/particle interaction. This affects the dispersion circumstance of the particles inside the composite and alters the electrical properties of the PTC composites.
- e. Modification of CB with metallic particles was following the purpose of reduction of room temperature resistivity in PTC composites prepared by them. The results showed that at lower content of Ni particles, CB denatured surface properties prevent formation of a suitable conduction network and resistivity increases. However, when the metal content on CB increases, substantial electrical conduction of the filler particles increases and thus, PTC system reaches to a resistivity even lower than its amount at room temperature.
- f. Results also showed a better compatibility between the HDPE matrix and Ni modified CB, in comparison to Au modified CBs. Higher room temperature resistivity and ambiguous phenomena observed for PTC samples prepared by Au modified CB is the supporting evidence for the latter statement.
- g. Annealing of the PTC samples made changes in their electrical properties. They showed a different response to annealing. Room temperature resistivity reduced after annealing for some of the samples while others showed an increase. This was attributed to the different types of the CB with different properties. Reaggregation of the conducting fillers and alternation of the crystalline properties of the matrix during the annealing process are believed to be the predominant factor in variation of room temperature resistivity after annealing.
- h. The most important changes which happened after annealing was the increase in PTC intensity of the composites. It is a commonly believed theory that during the heat treatment of the PTC materials, the matrix undergoes some improvements in its crystallinity and crystallite sizes. These lead to a different melting behavior of the matrix and thus affect the PTC phenomenon appearing around the melting point of the matrix. As evidence, T_g s also changes upon annealing of the PTC samples.
- i. The samples showed reasonable good adoption in electrical behavior based on thermal cycling between room temperature and above the T_g (140°C).

The authors thank the Research Department of Sahand University of Technology, which made this study possible.

References

1. Matsushige, K.; Kobayashi, K.; Iwami, N.; Horiuchi, T.; Shimomori, E.; Itoi, M. *Thin Solid Films* 1996, 273, 128.
2. Das, N. C.; Chaki, T. K.; Khastgir, D. *J Appl Polym Sci* 2003, 90, 2073.
3. Di, W.; Zhang, G.; Xu, J.; Peng, Y.; Wang, X.; Xie, Z. *J Polym Sci Part B: Polym Phys* 2003, 41, 3094.
4. Park, J. S.; Kang, P. H.; Young, C. N.; Dong, H. S. *J Appl Polym Sci* 2003, 89, 2316.
5. Yi, X. S.; Shen, L.; Pan, Y. *Compos Sci Technol* 2001, 61, 949.
6. Tang, H.; Chen, X.; Luo, Y. *Eur Polym J* 1997, 33, 1383.
7. Zhang, J. F.; Zheng, Q.; Yang, Y. Q.; Yi, X. S. *J Appl Polym Sci* 2002, 83, 3112.
8. Kim, J. I.; Kang, P. H.; Young, C. N. *J Appl Polym Sci* 2004, 92, 394.
9. Yu, G.; Zhang, M. Q.; Zeng, H. M.; Hou, Y. H.; Zhang, H. B. *J Appl Polym Sci* 1999, 73, 489.
10. Feng, J.; Chan, C. M. *Polymer* 2000, 41, 7279.
11. Heiser, J. A.; King, J. A. *Polym Compos* 2004, 25, 186.
12. Boiteux, G.; Fournier, J.; Issotier, D.; Seytre, G.; Marichy, G. *Synth Met* 1999, 102, 1234.

13. Feng, J.; Chan, C. M. *Polymer* 2000, 41, 4559.
14. Zhang, X. W.; Pan, Y.; Zheng, Q.; Yi, X. S. *J Appl Polym Sci* 2000, 78, 424.
15. Xie, H.; Deng, P.; Dong, L.; Sun, J. *J Appl Polym Sci* 2002, 85, 2742.
16. Lee, M. G.; Nho, Y. C. *Radiat Phys Chem* 2001, 61, 75.
17. Hou, Y. H.; Zhang, M. Q.; Rong, M. Z.; Yu, G.; Zeng, H. M. *J Appl Polym Sci* 2002, 84, 2768.
18. Kalyon, D. M.; Birinci, E.; Yazici, R.; Karuv, B.; Walsh, S. *Polym Eng Sci* 2002, 42, 1609.
19. Horita, K.; Nishibiri, Y.; Ohshima, T. *Carbon* 1996, 34, 217.
20. Paneta, D.; Darmstadt, H.; Kaliaguine, S.; Roy, C. *Appl Surf Sci* 2003, 217, 181.
21. Sosa, R. C.; Parton, R. F.; Neys, P. E.; Lardinois, O.; Jacobs, P. A.; Rouxhet, P. G. *J Mol Catal Part A: Chem* 1996, 110, 141.
22. Vogel, A. In *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed; Jeffery, G. H., Bassett, J., Mendham, J., Denney, R. C., Eds.; Longman Group Limited: Harlow, UK, 1989; p 693.
23. Chow, A.; Beamish, F. E. *Talanta* 1963, 10, 883.
24. Xue, Q. *Euro Polym J* 2004, 40, 323.
25. Hiramoto, M.; Nakayama, K.; Sato, I.; Kumaoka, H.; Yokoyama, M. *Thin Solid Films* 1998, 331, 71.
26. Tang, J. X.; Li, Y. Q.; Hung, L. S.; Lee, C. S. *Appl Phys Lett* 2004, 84, 73.
27. Medalia, A. I. *Carbon* 1986, 59, 432.
28. Bueche, F. *J Appl Phys* 1973, 44, 532.
29. Yacubowicz, J.; Narkis, M.; Benguigui, L. *Polym Eng Sci* 1990, 30, 459.
30. Miyayama, M.; Teranishi, J.; Yanagida, H. *J Mater Sci* 1993, 28, 6442.
31. Lee, G. J.; Suh, K. D.; Im, S. S. *Polym Eng Sci* 1998, 38, 471.
32. Hindermann-Bischoff, M.; Ehrburger-Dolle, F. *Carbon* 2001, 39, 375.
33. Luo, Y.; Wang, G.; Zhang, B.; Zhang, Z. *Eur Polym J* 1998, 34, 1221.
34. Zhang, M.; Jia, W.; Chen, X. *J Appl Polym Sci* 1996, 62, 743.