

Grafting of Poly(α -Chloroacrylonitrile) (α -PCIAN) on Carbon Black and Electrical Properties of α -PCIAN-Grafted Carbon Black Compositions

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Synopsis

The electrical properties of poly(α -chloroacrylonitrile) (PCIAN) carbon black compositions were determined. These materials were prepared by polymerizing α -chloroacrylonitrile in the presence of carbon black (GC resistors). Resistivities measurement of GC resistors shows a semiconductor-like behavior. Moreover, the resistance change of GC resistors with electrical field strength is very large. It is concluded that the conduction of GC resistors is controlled by the thin polymer layer present at the surface of the carbon black particles. Heat degradation of such compositions was also investigated: A significant weight loss above 150°C is observed in all cases which can be attributed to thermal dehydrochlorination of PCIAN. After heat treatment at 300°C, during 1 h, the resistivities decrease of about 1 order of magnitude because of the formation of a semiconducting polyconjugated polymer by dehydrochlorination of PCIAN.

INTRODUCTION

Conductive carbon black-polymer composite materials which have been widely studied,¹ are generally a combination of an insulating polymer and a carbon black.² Recently, many conducting polymers have been developed from such compositions and hence great practical interest exists for the preparation of such conductive materials.

This paper is concerned with the preparation and study of the electrical properties of carbon black-poly(α -chloroacrylonitrile) (PCIAN) composite, obtained by radical polymerization of α -chloroacrylonitrile in the presence of carbon black.

EXPERIMENTAL

Materials and Reagents

The carbon black used was Cabot XC 42 (BET specific surface area = 210 m²/g., geometrical specific surface area = 111 m²/g). α -Chloroacrylonitrile (99%) was purchased from EGA-Chemie Co.

TABLE I
 Polymerization Conditions of α -Chloroacrylonitrile in the Presence of Carbon Black^a

Sample	Monomer (g)	Carbon Black (g)	MEK (mL)	Reaction Time (h)	Polymer formed (g)	Conversion (%)	AIBN (mg)
G ₁	5.5	—	15	48	0.730	13.3	50[0]
G ₂	5.5	3.0	15[0] 10[2] 5[6]	48	1.221	22.2	50[0] 50[24]
G ₃	3.3[0] 3.3[24]	3.0	15[0] 10[2] 5[6]	72	1.920	29.0	30[0] 30[24]
G ₄	5.5[0] 5.5[24] 5.5[48]	3.0	15[0] 10[2] 5[48]	72	4.152	25.2	50[0] 50[24] 50[48]
G ₅	5.5[0] 5.5[24] 5.5[48] 5.5[72] 5.5[96] 5.5[120]	3.0	15[0] 10[2] 5[6] 5[48] 5[96]	144	9.543	28.9	50[0] 50[24] 50[48] 50[72] 50[96] 50[120]

^a Numbers in brackets indicate the time of addition of the product in hours: for start [0].

Polymerization of α -Chloroacrylonitrile^{3,4}

To a dispersion of 5 cm³ of α -CIAN in 20 cm³ of distilled water, in a 100 cm³ flask, were added 0.02 mol of ammonium persulfate used as initiator. The mixture was stirred, at 45°C, for 2 h in order to achieve the polymerization. The polymer was filtered, thoroughly washed with distilled water, dried under vacuum for 2 days, and stored in a desiccator. The conversion ratio was equal to 85%.

Polymerization of α -CIAN in the Presence of Carbon Black

Given weights of carbon black, α -CIAN, and α, α' -azobisisobutyronitrile (AIBN) which was used as the initiator, were dispersed in methyl isobutylketone (MBK). The mixture was heated at 70°C for the desired time under nitrogen. It was observed that grafting ratio of PCIAN remained at a low level for a single run; therefore supplementary amounts of α -CIAN, AIBN and solvent were added step by step, according to the conditions reported in Table I. Then, the mixture was poured into a large amount of a water-methanol mixture (volume ratio 9/1).

The precipitate was filtered, washed with distilled water, and oven-dried at 60°C. The percentage of polymer in the mix was calculated from chlorine and nitrogen contents (Table II), assuming that the nitrogen and chlorine contents of carbon black are negligible.

Extraction Test

Ca. 0.5 g of dried carbon black-polymer mixture was accurately weighted and submitted to extraction with acetone during 48 h in a Soxhlet. Then, the extracted product was dried under vacuum.

TABLE II
Characteristics of PCIAN-CB Compositions

Sample	%Cl	%N	%Cl/%N	%PCIAN	%PCNA ^a	%CB ^b	%CB ^c	% Extr.
G3	5.5	5.0	1.1	13.5	11.8	74.7	61	36.4
G4	17.5	9.7	1.8	43.1	11.7	45.2	42	49.4
G5	22.0	11.0	2.0	54.2	9.7	34.5	24	96.2
PCIAN	40.6	16.0	2.53	—	—	—	—	—

^a PCNA = polycyanoacetylene: $[-\text{CH}=\text{C}(\text{CN})-]_n$.

^b % of carbon black from elemental analysis.

^c % of carbon black from weight increase (weight of carbon black before and after grafting).

Preparation of Disklike Resistors

Disklike resistors were made by pressing at 10 ton/cm² for 1 h, ca. 600 mg of grafted carbon black, in an IR die cell.

Measurement of the Temperature Dependency of Resistivity

Temperature dependence of the resistivity of the samples was measured with a digital multimeter (Takeda Riken Industrial Co., Ltd., TR-6853). Resistivity against temperature curves, between -160°C and 100°C , were recorded by raising the temperature at a heating rate of $1^{\circ}\text{C}/\text{min}$.

Measurement of the Electrical Field Strength Dependence of Resistivity

Resistance changes versus electrical field strength were recorded according to the procedure described earlier.⁵ A given voltage was applied to the resistors in a pulse of 15 ms and the resulting current was measured.

Heat Treatment of PCIAN-Carbon Black Composite Materials

Samples were treated in an oven in a nitrogen atmosphere at the desired temperature, for a given time. Weight loss vs. temperature was also measured on the same samples with a thermobalance (Seiko Electronic Industrial Co., TG/DTA 30).

Electron Microscopy

Electron micrographs were obtained with an instrument (JXA-733) from Nippon Electron Co.

RESULTS

Grafting of α -CIAN on Carbon Black

Various initiators can be used^{3,4} for the polymerization of α -CIAN, but in the presence of carbon black their number becomes limited. Therefore, we used AIBN. Polymerization conditions are shown in Table I. To obtain polymer-grafted carbon black containing a high percentage of PCIAN, it was necessary to add supplementary amounts of monomer and initiator to the

reaction medium, certainly because of the inhibiting properties of carbon black. Further G5 was prepared by allowing the mixture to react for a prolonged period. When reaction approaches completion, the solution takes on a reddish black hue. Side reactions such as partial dehydrochlorination of PCIAN takes place in these conditions. The grafted carbon black, however, still disperses very well in a suitable solvent.

The percentage of chlorine and nitrogen determined by elemental analysis of the grafted samples are reported in Table II. The ratio between chlorine and nitrogen contents indicates clearly that an important dehydrochlorination process occurs during the polymerization. From chlorine and nitrogen contents, it is easy to calculate the respective percentages of α -PCIAN, of PCNA (polycyanoacetylene or dehydrochlorinated PCIAN) and of carbon black, in the composition. It is seen that the percentage of PCAN is quite independent of the preparation procedure of the product and that the stepwise addition of monomer increases only the amount of PCIAN and correlatively decreases the amount of carbon black in the mix. Hence, it is necessary to verify if the last added monomer is actually grafted as PCIAN on the carbon. Consequently, the samples were extracted with acetone in a Soxhlet extractor.

The percentage of extracted material is reported in the last column of Table II. In all cases, the percentages are significantly higher than the percentages of polymer determined by elemental analysis. The differences origin from the partial "extraction" of the grafted carbon black which was able to go through the sintered alumina cartridge during extraction. This phenomena was particularly important for the G-5 composition. Nevertheless, a clear correlation can be observed between the percentage of polymer and the percentage of extracted material. This point suggests that the major part of the PCIAN is not grafted on the surface of carbon black.

Finally, it is worth pointing out that the main part of PCAN is formed during the first steps of the polymerization as shown by the constant percentage of the PCAN, in all mixtures. PCAN possibly represents the nonextractable part of the composition, i.e., the one effectively grafted on the carbon surface. This observation suggests also that carbon black is indeed able to catalyze the dehydrochlorination of PCIAN which is in contact with its surface.

Study of Electrical Properties

Three disklike resistors were prepared from GC samples. The resistivities measured at room temperature are shown in the Table III. Relatively low values are recorded, a result which possibly results from fine dispersion of

TABLE III
Resistivities at Room Temperature of Resistors

Sample	Content of carbon black (%)	Resistivity (Ω cm)
R ₁	61	3.76
R ₂	42	6.73
R ₃	24	232



Fig. 1. Electron micrographs of PCIAN-carbon black composition: GC resistor R3 (from G5 [24% of CB]).

particles in the matrix. Indeed, electron microscopy (Fig. 1) indicates, for the GC resistor (R3) that carbon black particles can hardly be distinguished from the polymer matrix.

Influence of Temperature on the Resistivity of the Resistors

The variation of resistivity with temperature is illustrated in Figure 2. For GC resistors, the resistivity decreases with increasing temperatures. This behavior is typical of a semiconductor. Further, a very pronounced variation of the resistivity occurs around 0°C .

This observation may be brought in relation with those made by Hashimoto et al.⁶ who noted, for PCIAN polymers, a sharp increase in the lone pair radical concentration in the 250–270 K range. The decrease of the resistivity

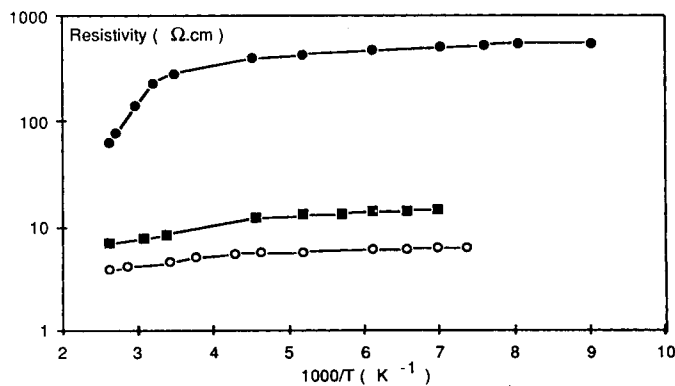


Fig. 2. Relationship between resistivity and $1/T$ for GC resistors: (●) R1 (from G3 [61% of CB]); (■) R2 (from G4 [42% of CB]); (○) R3 (from G5 [24% of CB]).

TABLE IV
Activation Energies of PCIAN-Carbon Black Composite Resistors

Sample	Activation energy below 0°C (eV)	Activation energy above 0°C (eV)
PCIAN	—	50×10^{-2}
R ₁	2.3×10^{-3}	1.0×10^{-2}
R ₂	4.4×10^{-3}	1.6×10^{-2}
R ₃	8.2×10^{-3}	19×10^{-2}

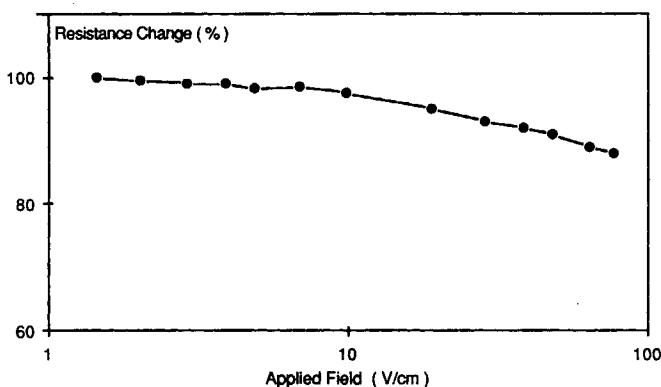


Fig. 3. Field dependence of resistance for GC resistor R3 (from G5 [24% of CB]).

of the GC resistors may well be accounted by the thermally activated process of the lone pair radicals formation.

From experimental curves, apparent activation energies for conduction mechanisms are calculated and the results are presented in Table IV. The activation energy for R3 is similar to that of PCIAN, i.e., the conduction is controlled by the polymer phase.

The corresponding values for R1 and R2, i.e., resistors made of more than 40% grafted carbon black, are lower than that of R3, but their activation energy changes around 0°C as does the one of the polymer.

Influence of Electrical Field Strength on the Resistivity

The variation of the electrical resistance characteristics with electrical field strength is given by Figure 3. Usually, the electrical resistance of carbon black polymer associations varies with increasing electrical field strengths. In the present case, the variation is very limited.

The dependence of the resistance on the electrical field strength is related to the gaps between carbon black particles as shown earlier.⁷

Influence of Thermal Degradation of PCIAN on Resistivity

The thermal degradation of PCIAN carbon black mixes was followed with a thermobalance (Fig. 4). Already, at 150°C, for all carbon polymer composites but also for pure PCIAN, a significant weight loss is observed. According to

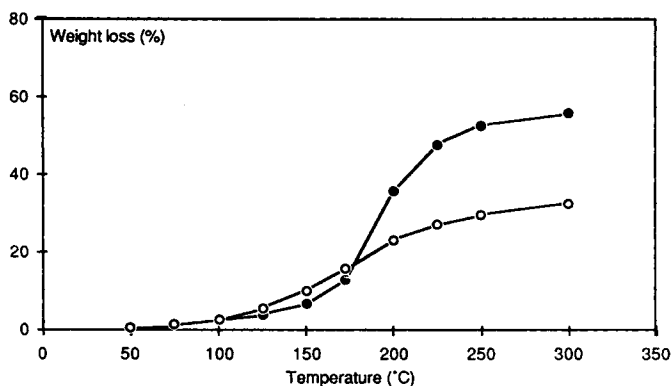


Fig. 4. Weightloss versus temperature of PCIAN and PCIAN-carbon black compositions: (○) PCIAN; (●) R3 (from G5 [24% of CB]).

Grassie and Grant⁴ the volatile material evolved below 150°C is principally water, but above this temperature, essentially hydrogen chloride is formed.

At the same time, a conjugated unsaturated bonds system is built. When increasing the carbon black content in the resistors, the weight loss resulting from the heat treatment is decreased.

Assuming that only the polymer phase is degraded, the weight loss on heating, taking pure polymer as a reference, is for PCIAN, 56% and for R3, 32%. The lower weight loss of the grafted resistor is easily explained knowing that the grafted polymer layer is in fact highly dechlorinated PCIAN as discussed before. The temperature dependence of R3, heat-treated for 1 h, at 300°C is shown by Figure 5. It appears that the characteristics of R3, after heat treatment, resemble those of R2.

An explanation is that the carbon black content of R3 is increased since part of the polymer is eliminated during the treatment. It is also noted that the activation energy for R3, after heat treatment is 0.04 eV, i.e., a value higher than that of any other mixed sample. It may be concluded therefrom that, in the case of GC type samples, the thin polymeric layers between carbon black particles remain even after heat treatment.

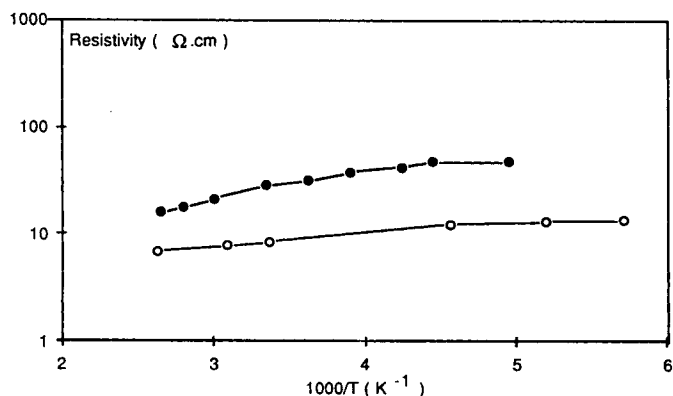


Fig. 5. Relationship between resistivity and $1/T$ for resistors: (●) R3 (from G5 [24% of CB]) heat-treated for 1 h at 300°C; (○) R2 (from G4 [42% of CB]) as reference.

CONCLUSION

Composite materials were prepared by polymerizing α -CIAN in the presence of carbon black. Grafted carbon black disperses readily in the polymer matrix whereas nongrafted carbon blacks usually form large aggregates. The resistivity of GC resistors is high. The temperature dependence resembles the one of a semiconductor and the resistance change with electrical field strength is important.

The conduction mechanism of GC resistors is controlled by the thin polymer layer between carbon black particles which are highly dispersed in the PCIAN matrix. After heat treatment at 300°C the resistivities of all compositions decrease by 1 order of magnitude, due to the formation of a semiconducting polymer (PCNA), which contains polyconjugated double bonds formed by thermal dehydrochlorination of PCIAN.

References

1. J. B. Donnet and A. Voet, *Carbon Black, Physics, Chemistry and Elastomer Reinforcement*, Dekker, New York, 1976.
2. K. Ohkita, *Carbon Black Grafted with Polymers*, Japanese Rubber Digest-sha Co. Ltd. 1982.
3. K. Kubushiro, M. Hatano, and S. Kanbara, *Kogyo Kagaku*, **67**, 1612 (1964).
4. N. Grassie and E. M. Grant, *J. Polym. Sci.*, **C-16**, 591 (1967).
5. S. Miyauchi, E. Togashi, Y. Sorimachi, and I. Tsubata, *Kobunshi Ronbunshu*, **40**, 195 (1983).
6. T. Hashimoto, M. Kinoshita, A. Takatu, and J. Shimizu, *Polym. Prepr.*, **31**(10), 2867 (1983).
7. S. Miyauchi and E. Togashi, *J. Appl. Polym. Sci.*, **30**, 2743 (1985).

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