

**CARBON
BLACK-
POLYMER
COMPOSITES**

**THE PHYSICS OF ELECTRICALLY
CONDUCTING COMPOSITES**

EDITED BY ENID KEIL SICHEL

Carbon Black-Polymer Composites

The Physics of Electrically Conducting Composites

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PREFACE

The study of composite materials is an intriguing area of materials science because composites often exhibit physical properties that are unlike those of their component materials. Furthermore, composites formed under different mixing conditions from identical starting materials may have dramatically different properties. Carbon-polymer composites are a good example. Composites made with carbon black, long used for elastomer reinforcement, have recently replaced metals in several industrial applications. Their usefulness depends on how well their properties can be manipulated, which in turn requires an understanding of the controlling physical mechanisms involved. Understanding the physical properties of the composite on a microscopic, quantum mechanical level is the key to exploiting the usefulness of these materials.

The emphasis in this book is on the electrical properties of carbon black-polymer composites. Included are the dc and ac conductivity at high and low fields and over a wide temperature range. A variety of carbon types and carbon loading levels are discussed, ranging from a small amount of carbon in which a doping mechanism of conduction is proposed to high carbon concentrations in which a tunneling mechanism of transport between carbon aggregates is proposed. All these studies depend on detailed materials characterization and an understanding of the morphology of the composite. The rheology of carbon polymer composites is a revealing compliment to the electrical properties, showing that the rheological properties depend on many of the same parameters that govern the electrical properties.

This work will be of interest to materials scientists, both industrial and academic. It represents a new examination, from a first-principles point of view, of a composite material whose elastic properties have long been appreciated.

I am indebted to my colleagues J. I. Gittleman and Ping Sheng. This book is an outgrowth of work begun with them at RCA Laboratories. The cheerful assistance of Joanne McLaughlin of GTE Laboratories is gratefully acknowledged.

Enid K. Sichel

INTRODUCTION

The electrical properties of carbon black-polymer composites have been appreciated by design engineers for years but have only recently been studied for a first-principles explanation of their properties. The origins of the recent interest can be traced to three sources: the interest in polymer physics of producing organic conductors; the study of composites of metals and insulators such as cermets, and the industrial use of carbon black-polymer composites in the capacitive video disk and in the xerographic process. The chapters in this book reflect the authors' interest in one or more of these areas. Together they provide a framework for understanding the physics of electrically conducting carbon black-polymer composites.

Chapter 1 contains a detailed analysis of the morphology and nature of carbon black by itself and as part of a carbon-polymer composite. The size of the individual carbon black particles, as well as their aggregate morphology and degree of dispersion, is the key to understanding the electrical properties of the composites discussed in the following chapters. Control of the surface chemistry of the carbon black, in practice, is critical to obtaining the type of composite desired, whether it is the electrical properties or the rheological properties (Chap. 6) that are most important.

Chapter 2 discusses a tunneling model for the electrical conduction in carbon black-polyvinyl chloride composites in which the carriers move across the gaps between carbon black aggregates and thermally generated voltage fluctuations play an important role in the tunneling process. The low-temperature electrical behavior is discussed in detail, in support of the model. Morphology and dispersion of the carbon black in the carbon-polymer composite govern the electrical properties.

Chapter 3 treats dc electrical properties that are of tremendous importance to the experimentalist in obtaining reliable information

about carbon black-polymer composites. A detailed analysis of contact resistance and contact space charge is presented to enable the reader to appreciate the subtle effects of ionic conduction on the electrical properties. The interaction of electronic and ionic conduction is explored as well as the origins of room temperature nonlinear current-voltage characteristics.

The physics of electrical conduction in the carbon-polymer composites treated in Chaps. 2 and 3 depends on a physical mixture of a conductor with an insulator in high enough proportions that electrons can either tunnel or percolate through a network of carbon black. Chapter 4 treats a novel carbon-polymer system in which the carbon black serves as a dopant in much the same way that semiconductors may be doped to enhance their conductivity. The dopant levels of carbon black are much lower than the levels discussed in the previous chapters. A model for the conduction process in carbon-doped polyesters is developed.

Returning again to physical mixtures of carbon black in carbon-polymer composites, Chap. 5 treats the ac electrical properties. The frequency dependence of the electrical conductivity is discussed, as is the effect of loading density of carbon black on frequency dependence. A model for the ac conduction is developed and compared with experimental results.

Compounding of conducting carbon-polymer composites presents a challenge to the materials scientist. The rheological properties discussed in Chap. 6 are related to the network of carbon in a conducting sample, just as the electrical properties are. The dispersion of the carbon black, which influences the electrical properties, is shown to have a profound effect on the mechanical properties of the composite. The characteristics of different carbon blacks are discussed in a manner that provides further insight into the nature of carbon black-polymer composites.

Chapter 7 covers the topic triboelectricity in carbon black-polymer composites. The physics of contact charging of carbon-polymer composites requires an understanding of surface phenomena and the influence of surface properties on the work function of various carbon blacks. [The effect of surface treatment of carbon black (absorption of oxygen, for example) on the electrical properties is analyzed in some of the earlier chapters.] The discussion of triboelectricity, a surface phenomenon, gives further depth to our understanding of carbon-polymer composites.

The various aspects of carbon black-polymer composites treated in each chapter complement each other and form a unified picture of the physics of carbon-polymer composites.

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NATURE OF CARBON BLACK AND ITS MORPHOLOGY IN COMPOSITES

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I. NATURE OF CARBON BLACK

A. General; Microstructure

Typical carbon blacks are composed of nearly pure carbon in colloidal entities of aciniform morphology. The term *aciniform*, meaning "clustered like grapes," refers to the characteristic appearance of the colloidal entities as composed of spheroidal *particles* fused together in clusters of branched, irregular shape (Fig. 1). The entities are gen-

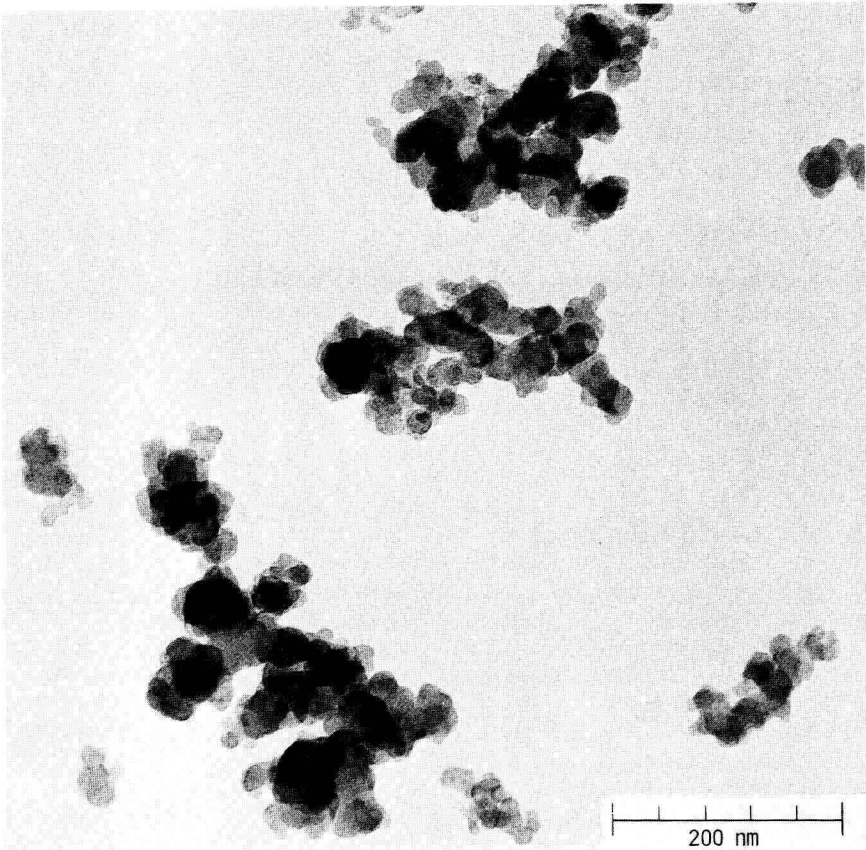


Fig. 1 Aggregates of reinforcing furnace black (N220).

erally called *aggregates*; the terms "primary aggregate," "kinetic unit," and "domain" have also been used. In a sense the aggregate is itself a colloidal particle, but the terminology indicated above has become well established in the carbon black literature and will be adhered to here. The spheroidal particles cannot be detached from the aggregates, but they are assumed to have existed independently (either as solid carbon or as viscous droplets) before fusion to aggregates.

Within each aggregate, the carbon atoms are arranged in imperfect graphite layers. The arrangement of carbon atoms and layers is referred to as *microstructure* [1]. As shown in Fig. 2, the layers are arranged more or less concentrically within each particle or growth center, with a fair degree of parallelism between adjacent layers in

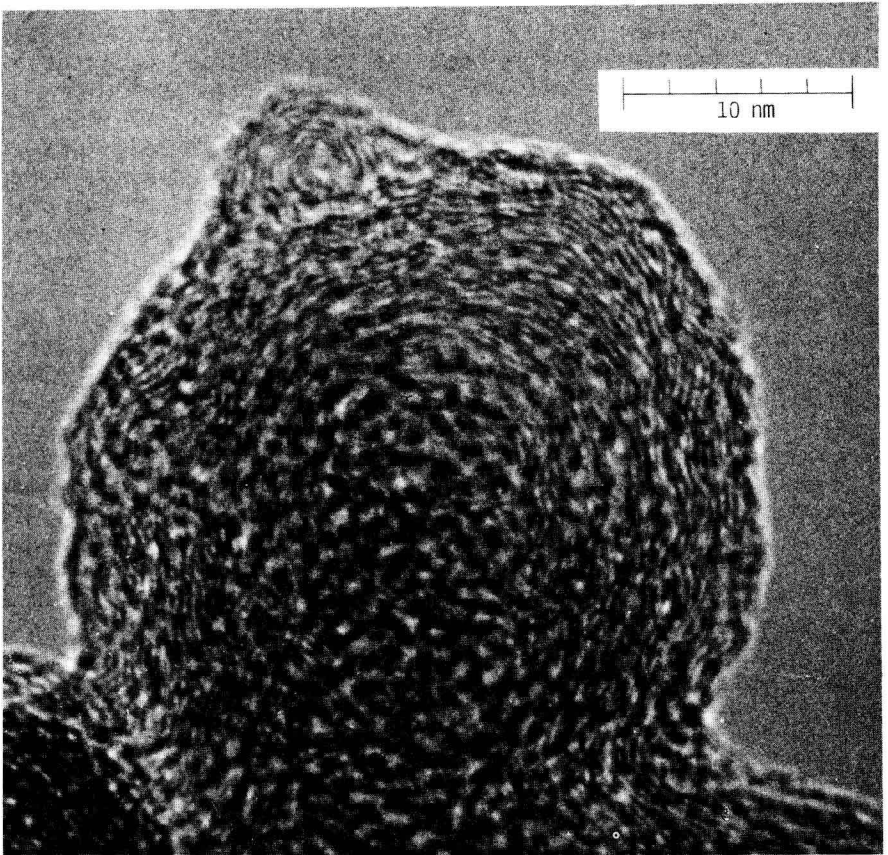
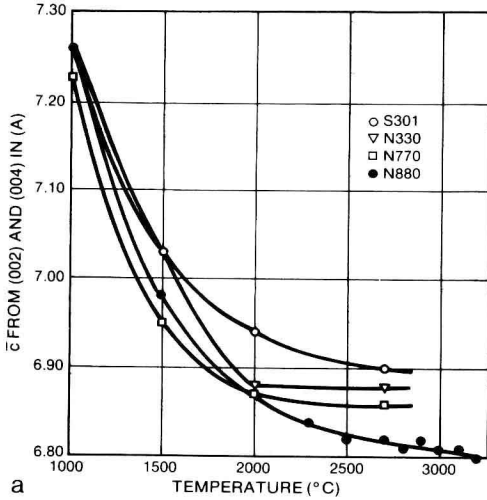
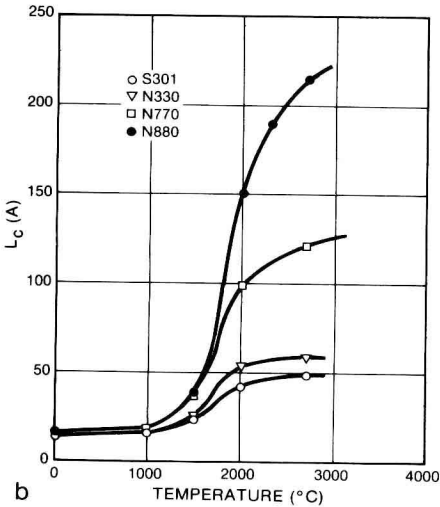


Fig. 2 Particle of reinforcing furnace black at ultrahigh magnification, illustrating concentric layer microstructure. Note secondary growth center of upper left and continuity of layers with rest of aggregate at bottom. (From Ref. 27).

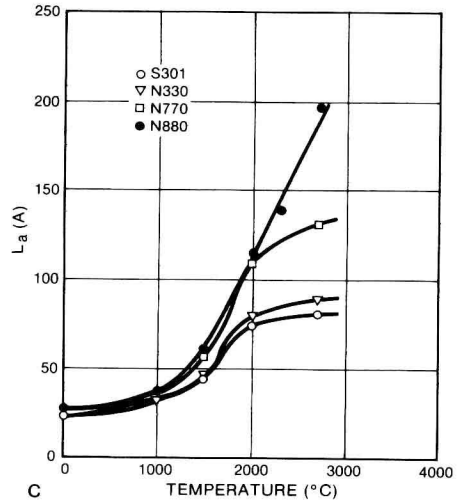
small regions or *crystallites*. The layers are continuous from one particle to the next within an aggregate [2]. The enhanced phase contrast of layers that are parallel to the electron beam accounts for the illusion of a section through the equatorial plane (Fig. 2). However, because of imaging problems in high-resolution electron microscopy [3,4], the electron micrograph is only an approximate rendition of the actual arrangement of layers. Features such as forked or zigzag layers, which are visible in the electron micrograph, may be artifacts of the imaging process; even the apparent number of layers in a crystallite may be altered somewhat by the imaging process [4].



a



b



c

Fig. 3 a: Average interlayer spacing versus 2h HTT. Note: \bar{c} = twice the interlayer spacing (002 d). b: Apparent crystallite thickness, L_c , versus 2h HTT. c: Apparent layer dimension, L_a , versus 2h HTT. (Reprinted with permission from Ref. 8, © 1953, American Chemical Society.)

Abrupt bending of layers appears to be real, however, and has been attributed to tetrahedral bonding [5]. Imaging of isolated layers is especially poor, so electron microscopy cannot reveal if any such layers may be protruding from the surface.

X-ray diffraction studies of typical blacks₀ have shown an inter-layer distance (002 d spacing) of 3.5 to 3.65 Å as compared with 3.354 Å for graphite [1,6,7]. The increased d spacing is due to the fact that the layers are not in register but are simply parallel with no three-dimensional ordering; this is called *turbostatic*. Typical measured dimensions, $L_c = 15 \text{ \AA}$ and $L_a = 20 \text{ \AA}$, must be interpreted with caution in view of the imperfect, paracrystalline microstructure. The layers are probably larger than indicated by the value of L_a , but contain defects that reduce the measured value of L_a . Since x-ray diffraction gives mass-average values, it cannot give information about the surface layers, nor can it indicate the spatial distribution of properties within the aggregates. Oxidation studies suggest that the interior of the particles is less well organized, or contains more defects, than the region at or near the surface.

Carbon blacks made by the furnace process (*furnace blacks*, Sec. I.E) are formed at temperatures of 1200 to 1800°C, higher temperature and shorter residence time being associated with finer particle size. Because the residence time at these temperatures is very short (5 to 100 ms, depending on the grade), and because the material is not fully carbonized until near the end of this short period, the carbon has not attained the microstructure characteristic of prolonged heating at these temperatures. When a carbon black is heated in the absence of oxygen at heat treatment temperatures (HTT) above 1000°C, progressive annealing and growth of the graphitic layers takes place, as shown by x-ray diffraction (Fig. 3), accompanied by changes in surface area properties [8]. A practical limit of heat treatment is reached at about 2700°C since at higher temperatures the rate of vaporization becomes appreciable and the carbon black may become contaminated by carbon redeposited from the vapor in cooler regions of the apparatus. Heat treatment at about 2700°C is referred to as *graphitization*, although the three-dimensional ordering of graphite is not developed. Before heat treatment, the small size of the layers and the numerous imperfections allow little driving force for the layers to become aligned in register; in the heat-treated or graphitized black, the constraints imposed by the aciniform morphology apparently prevent such alignments. As shown in Fig. 4, the appearance of a carbon black aggregate is dramatically altered by graphitization, with development of a hollowed, capsular morphology; yet the particle size is retained at least approximately, as shown also by the small (14%) change in the surface area measured by gas adsorption. In the past, an S301 carbon black (Spheron 6), made by the now-obsolete channel process, was heated to 2700°C to make Graphon, which was widely used in adsorption studies. At present, a similarly heated-treated furnace