Electrically Conductive Organic Polymers for Advanced Applications

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ELECTRICALLY CONDUCTIVE ORGANIC POLYMERS FOR ADVANCED APPLICATIONS

by

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Foreword

This book is a study of electrically conductive organic polymers for advanced applications. The properties of electrically conducting, semiconducting, and semi-insulating polymers were surveyed and their conduction mechanism, mechanical properties, and suitability for space-based use evaluated. Correlations between molecular structure, conductivity, and mechanical properties were drawn, and a comprehensive model of electrical conductivity in organic polymers was formulated.

The environmental exposure of polymer dielectrics used in spacecraft to high-energy electrons results in the accumulation of secondary electrons. When the electrostatic potential resulting from the accumulated charge exceeds the dielectric strength of the polymer, a breakdown occurs that can interrupt or damage normal function. This charging phenomena could be eliminated if dielectrics with a moderate electrical conductivity were used. At high potentials, charge would be drawn off at a higher rate than electrons are accumulated, thus preventing discharge. A successful material for the moderation of charging problems would thus possess a moderate resistivity and the other properties required for space-based use, including mechanical integrity, environmental resistance, and long-term stability.

Although the most widely studied electrically conducting polymers are not robust enough for most space-based uses, several commercial materials appear to have the necessary combination of electrical, thermal, and mechanical properties. The main obstacle to the selection of new or modified materials for spacecraft use is the lack of strength, thermal stability, and radiation resistance—not their conductivity. Several synthesis procedures are identified that would raise the value of these properties to acceptable levels for materials that have the required electrical properties.

The wide range of data reported in the literature can be reconciled by a theory of conductivity in which the limiting feature is the rate at which electrons are transferred between localized charge states. Variations in chemical structure lead to changes in the relative energy of the charge states and their relative orientation, but high mobilities are observed only in systems that form a periodic superlattice, of localized states. Some of the new polymers identified by this model have been prepared. They possess relatively high electrical conductivities and, unlike the majority of electrically conducting polymers, are processable in organic solvents. Although prepared for space applications, this book has obvious commercial implications. The chemical and polymer industries should benefit considerably from this book, as it places between covers the appropriate theory and technology, as well as brings together data regarding the electrical conductivity of about 250 polymers. The book is a very good guide to current technology, and future applications.

The information in the book is from *New Polymeric Materials Expected to Have Superior Properties for Space-Based Uses,* prepared by David B. Cotts and Zoila Reyes of SRI International for Rome Air Development Center Air Force Systems Command, July 1985.

The table of contents is organized in such a way as to serve as a subject index and provides easy access to the information contained in the book.

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NOTICE

Contents and Subject Index

1. Introduction

The environmental exposure of polymer dielectrics used in spacecraft to high energy electrons results in the accumulation of secondary electrons. When the electrostatic potential resulting from the accumulated charge exceeds the dielectric strength of the polymer, a breakdown occurs that can interrupt or damage normal spacecraft function. This spacecraft charging phenomena could be eliminated if dielectrics with a moderate electrical conductivity were used. At high potentials, charge would be drawn off at a higher rate than electrons are accumulated, thus preventing discharge.

A successful material for the moderation of spacecraft charging problems would thus possess a moderate resistivity, assumed to be about 10^{12} ohm cm, and the other properties required for space-based use, including mechanical integrity, environmental resistance, and long-term stability.

The purpose of this report is to formulate a coherent theory of conduction in polymers to allow the identification of materials that have resistivities less then 10^{12} ohm cm and that meet other requirements for spacecraft use. The report structure is as follows: In Section 2 we summarize our results and conclusions. The following two sections (3 and 4) deal with the contemporary use of polymers in spacecraft and discuss the effects of the radiation found in the spacecraft environment on the properties of polymers. The known conducting and semiconducting polymers are discussed in Section 5 and their suitability for use in space is discussed in Section 6. The next two sections summarize contemporary models of the conduction process (Section 7) and present a generalized model for conduction in organic polymers (Section 8). The final two sections (9 and 10) discuss the implications of this model on the design of new or modified electrically conducting polymers and the important questions concerning polymer conductivity that remain to be answered by future research.

Each of these sections is largely self-contained. We hope that, for example, an engineer can use the results of our material evaluation in Section 6 without becoming embroiled in the polymer structures presented in Section 5 or the discussion of polymer conductivity in Section 7. Similarly, we hope that the chemical community will benefit from our conclusions concerning structure-property relationships in Chapter 9 without necessarily digesting the information about the applications of polymers discussed in Section 3. For convenience, our results and conclusions are summarized in the following section.

2. Summary and Conclusions

Despite the extensive range of polymer compositions and structures that have been investigated over the last 50 years, there is no good theoretical model for conductivity or empirical correlation between polymer structure and electrical conductivity. One reason for this is that polymers possess a heterogeneous degree of inter- and intramolecular order. Good models exist for crystalline and amorphous semiconductors which represent two extremes in structural order. However, no good model exists for materials with intermediate degrees of order.

Various polymer conductivity phenomena can be explained by introducing the inhomogeneous transport of charge through ordered regions with periodic differences in composition. These disparate phenomena include the dramatic effect of oxidizing agents or dopants on conductivity, mobilities ranging over 10 orders of magnitude, a metallic thermopower, and a temperature dependence of the conductivity indicative of a variable-range hopping mechanism.

In spacecraft applications a relatively small set of commercial materials are used to fulfill a specific set of functional requirements. Generally, the relationships between molecular structure and material property (e.g., thermal stability, radiation resistance, strength) are better known than the dependence of conductivity on structure, so there is considerable lattitude in which to design new materials or to modify known polymers. To identify these modifications, we have brought together data reported in the literature concerning the molecular structure and electrical conductivity of nearly 250 polymers. These data indicate that inhomogeneous transport between localized states is responsible for the temperature, dopant, processing, and structure dependence of conductivity in organic polymers. The structural features favoring conductivity include:

- A polymer backbone containing medium-range (10-50 Å) electron delocalization.
- Molecular orbital structures capable of stabilizing radical ions, particularly heteroaromatic rings containing nitrogen and sulfur.
- Few or no pendant groups to interfere with close intermolecular packing and alignment.
- Ability to form partially oxidized (or reduced) complexes with intercalated low molecular weight species.

On the basis of these general descriptions, several contemporary or readily modified materials have been identified that we believe have the requisite conductivity to reduce spacecraft charging and the physical properties necessary for application in spacecraft.

One example is polyvinylcarbazole (PVK), which has good thermal stability, radiation resistance, mechanical properties, and is a good semiconductor. It has been extensively investigated as a photoconductor and can be doped with additives or its molecular structure can be altered to control its conducting properties. Development of more highly stereoregular PVK could increase its thermal stability by 50° to $100^{\circ}C$, making it useful as a primary structural material for direct exposure to the space environment.

A second potential class of materials are the pyropolymers including pyrolyzed polyacrylonitrile (PAN), pyrolyzed aromatic polyimides (e.g., Kapton), and polyacene quinone radicals (PAQRs). The electrical properties of pyrolyzed PAN and Kapton have been studied in some detail. Although their molecular structure after pyrolysis is relatively unknown and very little mechanical property data are available in the literature, they appear to be of considerable potential in reducing spacecraft charging phenomena. Carbonized PAN fibers are the primary source of high-strength carbon fiber, which is widely used in the aerospace community, so it is reasonable to believe that a pyrolyzed PAN or polyimide would have significant strength and stability. Kapton film and other polyimide resins are already used in aerospace vehicles and valued for their strength, radiation resistance, and thermal stability.

A third possibility is the use of modifications of the four most highly conducting polymers: polythiazyl (SN_x), polypyrrole (PP), polyphenylene sulfide (PPS), and polyacetylene (PA). The high conductivities of these materials in their doped "metallic" state are indicative of an electron delocalization that is incompatible with chemical or thermal stability. Undoped materials display nearly semiconducting (10^{10}-10^{12} ohm cm) resistivities that are believed to be adequate for protection from spacecraft charging. Very little mechanical property data are available for these materials, and more work needs to be done if they are to be qualified for spacecraft use.

Finally, there are new polymer compositions that meet the four criteria summarized on the previous page. We explored the synthesis of these compounds and have found several that have the desired electrical properties in addition to being mechanically strong, stable, and easily processed into films, fibers, and castings. Many of these polymers are structurally similar to the more radiation-resistant polymers and may represent a new class of materials for use in minimizing the problem of spacecraft charging.

This study has uncovered many questions concerning conductivity in organic polymers, its relation to molecular structure, and its application to problems as diverse as spacecraft charging, and molecular electronic devices. The basic methodology used (i.e., correlating molecular structure with mechanical, thermal, and electrical property data) has provided guidelines for the selection of spacecraft materials and insight into the mechanisms responsible for polymer conductivity

3. Polymer Use in Spacecraft

This section consists of three parts. The first describes the general applications in which polymers are used in spacecraft to illustrate the diversity of materials and properties encountered. The second contains a set of generic material requirements for each of the applications discussed. Although these descriptions may not be exact for each possible example, they provide a set of baseline properties for comparison with new materials. The third section summarizes the types of commercial materials used in these applications. In reading material specifications, one is struck by the fact that although many formulations may contain a readily available polymer (e.g., polystyrene), few materials with alternative molecular structures and comparable thermal and mechanical properties have been evaluated.

Our objective in preparing this section was to provide the reader with a functional description of specific applications, an example of the materials used, and a sense of the range of molecular structures that could be used. The following text is an introduction to the bulk of the data in Appendices A through E.

Functional Applications of Polymers

A series-by-series (e.g., Explorer, Pioneer, Nimbus) description of the polymeric materials used in spacecraft can be found in the Space Materials Handbook,[1] which illustrates five general categories of applications:

- Structural polymers including films, casting resins, fibers, and matrix resins.
- Electronic applications including insulation, circuit boards encapsulants, and standoffs.
- Adhesives, sealants, and elastomers.
- Lubricants, both solid and liquid.

- Thermal control including insulation and radiative surface coatings.

Material Requirements

The use of organic polymers in structural applications is increasing rapidly because of significant weight savings. Concomitant advances in the development of thermoset and thermoplastic resins with improved high temperature/environmental resistance are just beginning to have an effect on the design of aerospace components. Load-bearing structures (e.g., booms, spars, vertical and horizontal stabilizers) typically are expected to possess tensile strengths of 100 MPa, moduli of 3,000 to 5,000 MPa, heat distortion temperatures in excess of 500 K and compressive and shear strengths of from 50 to 100 MPa. In these structural roles, both unfilled resins and fiber-reinforced resins display strains-at-break of 2% to 5% and low ($< 10^{-5}$) thermal expansion coefficients. A wide range of polymers is used in secondary structural roles for which moderate strengths (20-50 MPa) and moduli (500 to 1000 MPa) are required and strains-at-break of up to 5% are encountered. The temperature extremes to which these structures are exposed is narrower, from 150 to 350 K, approaching the glass transition or heat distortion temperatures. Although for most purposes these polymer materials can be considered as insulators, environments where exposure to ionizing radiation is severe require more careful distinctions to be drawn. Tolerance to exposures exceeding 10^9 rads without significant degradation is generally required for spacecraft materials. These distinctions are particularly important in the choice of materials whose primary function is to perform as an insulator or other dielectric material.

Polymers for thermal control include fairly specialized functions such as thermal insulators, ablative materials, and surface coatings to maximize the reflection of sunlight and the radiative cooling of the satellite. Thermal stability, heat capacity, and thermal conductivity are of primary concern in these materials. Mechanical properties are of secondary concern since these materials are usually applied as