

IntechOpen

Electrical and Electronic Properties of Materials

Edited by Md. Kawsar Alam



ELECTRICAL AND ELECTRONIC PROPERTIES OF MATERIALS

Edited by Md. Kawsar Alam

Electrical and Electronic Properties of Materials

http://dx.doi.org/10.5772/intechopen.73110 Edited by Md. Kawsar Alam

Contributors

Turgut Ozturk, Muhammet Tahir Guneser, Fatima Ternero, Juan Manuel Montes, Francisco G. Cuevas, Jesús Cintas, Eduardo S. Caballero, Wieslawa Urbaniak-Domagala, Jianying Li, Kangning Wu, Yuwei Huang, Md. Kawsar Alam

© The Editor(s) and the Author(s) 2019

The rights of the editor(s) and the author(s) have been asserted in accordance with the Copyright, Designs and Patents Act 1988. All rights to the book as a whole are reserved by INTECHOPEN LIMITED. The book as a whole (compilation) cannot be reproduced, distributed or used for commercial or non-commercial purposes without INTECHOPEN LIMITED's written permission. Enquiries concerning the use of the book should be directed to INTECHOPEN LIMITED rights and permissions department (permissions@intechopen.com). Violations are liable to prosecution under the governing Copyright Law.

CC BY

Individual chapters of this publication are distributed under the terms of the Creative Commons Attribution 3.0 Unported License which permits commercial use, distribution and reproduction of the individual chapters, provided the original author(s) and source publication are appropriately acknowledged. If so indicated, certain images may not be included under the Creative Commons license. In such cases users will need to obtain permission from the license holder to reproduce the material. More details and guidelines concerning content reuse and adaptation can be foundat http://www.intechopen.com/copyright-policy.html.

Notice

Statements and opinions expressed in the chapters are these of the individual contributors and not necessarily those of the editors or publisher. No responsibility is accepted for the accuracy of information contained in the published chapters. The publisher assumes no responsibility for any damage or injury to persons or property arising out of the use of any materials, instructions, methods or ideas contained in the book.

First published in London, United Kingdom, 2019 by IntechOpen eBook (PDF) Published by IntechOpen, 2019 IntechOpen is the global imprint of INTECHOPEN LIMITED, registered in England and Wales, registration number: 11086078, The Shard, 25th floor, 32 London Bridge Street London, SE19SG – United Kingdom Printed in Croatia

British Library Cataloguing-in-Publication Data A catalogue record for this book is available from the British Library

Additional hard and PDF copies can be obtained from orders@intechopen.com

Electrical and Electronic Properties of Materials Edited by Md. Kawsar Alam p. cm. Print ISBN 978-1-78984-929-5 Online ISBN 978-1-78984-930-1 eBook (PDF) ISBN 978-1-83881-717-6

We are IntechOpen, the world's leading publisher of **Open Access books** Built by scientists, for scientists

Open access books available

3,900+ 116,000+

International authors and editors

120M+

Downloads

15 Countries delivered to

Our authors are among the lop 1% most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science[™] Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



Meet the editor



Dr. Md. Kawsar Alam is an Associate Professor with the Department of Electrical and Electronic Engineering at Bangladesh University of Engineering and Technology (BUET). He obtained his PhD in Electrical and Computer Engineering from The University of British Columbia (Vancouver), Canada in 2011. He has authored more than 40 scientific articles including a book chapter and

leads the Nanoscale Science and Technology Research Group at BUET. His research areas lie within the intersection of applied physics, electronics, and materials science. His current research interests include Materials Science, Nanoscale Device Modeling and Simulation, Nano-Electro-Mechanical Systems (NEMS), Photovoltaic Devices, Ab-initio Modeling and Simulation, Molecular Dynamics, Charged Particle Interaction with Nano-materials, Electron Emission Properties of Nanostructures, and Monte Carlo Simulation.

Contents

Preface XI

Section 1	Introduction 1
Chapter 1	Introductory Chapter: Electrical and Electronic Properties of Materials 3 Md. Kawsar Alam
Section 2	Properties of Porous Compacts, Polyesters and Ceramics 9
Chapter 2	Electrical Resistivity of Powdered Porous Compacts 11 Juan Manuel Montes, Francisco Gómez Cuevas, Jesús Cintas, Fátima Ternero and Eduardo Sánchez Caballero

- Chapter 3 Electrical Properties of Polyesters 35 Wieslawa Urbaniak-Domagala
- Chapter 4 Breakdown Characteristics of Varistor Ceramics 59 Jianying Li, Kangning Wu and Yuwei Huang
- Section 3 Measurement Methods and Extraction Techniques 81
- Chapter 5 Measurement Methods and Extraction Techniques to Obtain the Dielectric Properties of Materials 83 Turgut Ozturk and Muhammet Tahir Güneşer

Preface

Materials are broadly categorized as metals, insulators, or semiconductors. They are the basic building blocks of today's technologies. Modern science and technology requires control over the properties of materials so that they may be applied to different applications. The multidisciplinary nature of the materials science has attracted researchers from all sorts of fields and led to the discovery of many novel materials as well as the concept of man-made meta-materials. To name a few among the vast classes of materials: crystalline, polycrystalline, dielectrics, polymers, ceramics, superconductors etc. are widely used. Thus, when the IntechOpen editors invited a proposal for a book project, it was natural for me to propose one on the properties of materials.

This book is not an introduction to materials science or properties, rather it is an advanced level book on the properties of metal powder systems, polyesters, and varistor ceramics. It requires knowledge of applied physics, electronics, and some engineering. There are five chapters and the first one, the introductory chapter, summarizes the content of the contributed chapters. Among them, there is one contributed chapter on the measurement methods and extraction techniques that are employed to inherit the dielectric properties of dielectric materials. The contributed chapters have been selected from more than twenty proposals. The targeted audience of this book is senior undergraduate and graduate students. We believe that the contributions would be of interest to physicists, chemists, and of course to material scientists and engineers.

Chapter 2 discusses different models of electrical resistivity of powdered porous compacts. The proposed empirical models are compared with experimental data where necessary to justify the modeling parameters. Chapter 3 answers one interesting phenomenon: how polyester behaves under a DC field? The potential of changing the innate electroinsulating properties of polyester to impart electroconductive and antistatic properties is also investigated in this book. Chapter 4 presents the properties of varistor ceramics under different doping mechanisms. The ultimate goal is to improve the breakdown characteristics of the ceramics, which has applications in power systems and protection circuits. The last chapter focuses on different techniques has been made and the prospects of free space measurement method in measuring material properties in THz frequency range are discussed.

During the editing of this volume, I have received full support from IntechOpen that I must acknowledge, and encouragement from my colleagues, directly or indirectly. I would like to specially mention one graduate student's name, Ms. Mahnaz Islam, who has helped me in finalizing the introductory chapter. I would also like to thank my other research group members and express deep gratitude to my family without whose support this book would not have been possible.

> Md. Kawsar Alam Department of Electrical and Electronic Engineering Bangladesh University of Engineering & Technology Dhaka, Bangladesh

Section 1

Introduction

Introductory Chapter: Electrical and Electronic Properties of Materials

Md. Kawsar Alam

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.82360

1. Introduction

Materials science is an interdisciplinary field having common interest to physicists, chemists, and engineers. Understanding the basic principles and properties of materials has been one of the most challenging attempts of mankind. Researches starting from apprehending a single atom to bulk materials such as metals, insulators, and semiconductors have led us to the point of current technological revolution. In this fascinating endeavor, electrical and electronic properties of matters have played a crucial role.

Properties from microscopic such as (but not limited to) band structure to macroscopic resistivity, conductivity, effective mass, permittivity, etc. are of immense interest to the materials scientists. Theoretical and experimental analyses of such characteristics are inevitable before employing different materials such as nanotube, polymer, ceramics, porous compacts, etc. in different fields of engineering.

2. Content Overview

There are many basic textbooks on the fundamental concepts of materials. This book is more specifically aimed to special materials that are of current interests. It is not possible to cover all the emerging materials and their properties in a small book. Still, the content of this concise yet complete enough book covers polyesters, varistor ceramics, powdered porous compacts, and some measurement and parameter extraction methods of dielectric properties. These classes of materials are of interest to materials scientists as well as to engineers, physicist, and chemist or other related fields. There are four contributed chapters in this book. Each class of materials as mentioned above is explained with reference to experimental works or real-world examples.



© 2018 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Researchers have been intrigued about the electrical conductivity of porous materials and been trying to cite its causes by studying it from various angles [1–6]. Model equations with empirical parameters to estimate the effective resistivity of metal powder systems are presented. It is shown that the effective electrical resistivity can be estimated from the material resistivity and the porosity degree of the sample and of the tap porosity of the starting powders. The validity of proposed equations has been experimentally justified with reasonably good agreement between experimental and fitted theoretical values. The equations would be useful to describe the early stages of electrical consolidation techniques. Electrical activation process has also been described based on the presented models, which may be useful to describe dielectric breakdown process of oxide layers.

During the last decade, polyesters, which include biodegradable and conventional polymers, have been under the limelight of interdisciplinary research [7, 8]. Their wide variety of applications in diverse arenas such as medical, ecological, and agricultural have attracted researchers from wider disciplines. Futuristic applications enabled by the chemical as well as physical metamorphosis of polyesters have also propelled their studies in different research fields. This has begged many questions regarding the behavior of polyesters under different electrical phenomena, which are yet to be answered. One such question, covered in this book, demands the analysis on behavior of polyester under a DC field [9].

In particular, the characteristics of aliphatic-aromatic polyesters such as poly(ethylene terephthalate) (PET), polycarbonate (PC), and aliphatic polyester such as poly(lactic acid) under an applied DC field are analyzed. The microstructure of polymers has important consequences for their electric properties as addressed in this book. For instance, electrets are materials which can retain a permanent electric charge, and the susceptibility of polymers to polarization enables their use as electret materials. As such, the electrical conductivity of poly(ethylene terephthalate) films in a DC field is discussed. Among other factors, the relative humidity of the medium is known to affect the properties of polymer films such as poly(ethylene terephthalate) [7, 10]. To address this notion, the electrical conductance of poly(ethylene terephthalate)based products under different relative humidities in a DC field is studied.

In modern processing, the most common deposition techniques include physical vapor deposition (PVD) [11] and chemical vapor deposition (CVD) [12]. The potential of changing the innate electroinsulating properties of polyester fabrics via the use of these techniques as well as digital printing [13] to impart electroconductive and antistatic properties is also investigated in this book. In particular, studies on the contact electricity in the PET film and various metal systems are presented. A potential use of polyester fabrics in packaging is often hindered by its susceptibility to static electricity. The intent of this investigation is to reduce the risk in this potential use and also introduce new range of applications for polyester fabrics by extending its functionalization.

Another class of materials, varistor ceramics, has made their mark for applications in power system and protection circuits, which can be traced back to their excellent nonlinear current–voltage characteristics [14–16]. However, keeping in trend with the miniaturization of electronic devices, it has become imperative to improve the breakdown characteristics of existing varistors. It is known that the breakdown field is majorly affected by single grain boundary

characteristics, as determined by Schottky barriers and the amount of grain boundaries in the direction of the electric field [17, 18]. In this book, different doping techniques are introduced to improve the microstructure of varistors, in particular ZnO varistor ceramics and perovskite CaCu₃Ti₄O₁₂ (CCTO) ceramics, and to result in enhanced breakdown performance. Precisely, the electrical breakdown field is increased in Ca_{1-x}Sr_xCu₃Ti₄O₁₂ ceramics via tailoring donor density and CCTO-xCuAl₂O₄varistor ceramics synthesized in situ. Enhanced nonlinear electrical characteristics are obtained in CCTO-YCTO composite ceramics prepared with solid-state reaction method. The improvement in breakdown characteristics is attributed to the control of defect structure of Schottky barrier at grain boundaries and restricted grain size.

Besides their microstructure, the electrical performance of varistors has also been reported to vary within the bulk of the ceramic. Dimensional effect presents as the variation of the breakdown field in varistor ceramics with its thickness [19, 20]. It has been found that both the breakdown field and the nonlinearity in electrical characteristics decrease alarmingly as the thickness decreases beyond a critical limit. Investigating the origin of dimensional effect in varistor microstructures both theoretically and experimentally, the uniformity of grain sizes is found to have major consequences for the dimensional effect observed in ZnO ceramics as well as CCTO ceramics. To provide solid evidence for the idea, experimental efforts are made to eliminate dimensional effect in the aforementioned varistor ceramics by controlling grain sizes. Indeed, restrictions in grain sizes and their subsequent narrower distribution have allowed the observed dimensional effect to diminish.

The last chapter of this book focuses on the different measurement methods and extraction techniques that are employed to inherit the dielectric properties of dielectric materials. To facilitate increasingly novel applications in microwave, mm waves, and THz frequency range, accurate and precise knowledge of material properties is essential, which drives focus onto material characterization and appropriate measurement and extraction methods [21–23]. A particular dichotomy of the vast numbers of measurement methods can be into upconversion, such as a microwave or mm wave measurement method aimed at increasing frequency from 10¹⁰ to 10¹¹ Hz, and downconversion to decrease the frequency from 10¹⁴ to 10¹² or 10¹¹ Hz. Important dielectric properties, such as complex permittivity and refractive index, are used for presenting the comparison and analysis in this study. A comparison is made between the expensive THz time-domain spectroscopy (THz-TDS) system and multimode laser diode (MLD) for TDS systems [24], where advantages of the latter are discussed theoretically and experimentally. The prospects of free space measurement method, traditionally labeled as a microwave measurement method, in measuring material properties in THz frequency range, are discussed.

Poor extraction of data from measurements made with high accuracy can also present as a hindrance to precise material characterization. In that regard, different calibrating and extraction techniques are applied to measured data in this chapter to establish a comparison between them. Extraction of the complex permittivity and permeability of the materials is enabled by scattering parameters using analytical, for instance, Nicolson-Ross-Weir (NRW), and numerical extraction techniques such as Newton-Raphson method [25]. Keeping with recent trends, the idea of using artificial intelligence (AI) methods to bolster numerical techniques in extracting the dielectric properties is also put forward [26].

3. Summary

Advanced knowledge in materials science is essential, particularly since, at the present time, scientific innovation in this area has excelled beyond expectations. This work serves that purpose very well. The content of this book is not only extremely appropriate for engineering students, material scientists, physicists, chemists, etc. but also equivalently beneficial to those who pursue this field in the industry.

Author details

Md. Kawsar Alam

Address all correspondence to: kawsaralam@eee.buet.ac.bd

Department of Electrical and Electronic Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

References

- Einstein A. EineneueBestimmung der Moleküldimensionen. Annals of Physics. 1906; 19:289-306
- [2] Fricke H. A mathematical treatment of the electric conductivity and capacity of dispersed systems. Physical Review. 1924;24:575-587
- [3] Murabayashi M, Takahashi Y, Mukaibo T. Effect of porosity on the thermal conductivity of ThO₂. Journal of Nuclear Science and Technology. 1969;**6**:657-662
- [4] Schulz B. Thermal conductivity of porous and highly porous materials. High Temperatures-High Pressures. 1981;13:649-660
- [5] Stauffer D, Aharony A. Introduction to Percolation Theory. London: Taylor and Francis; 1994
- [6] Euler KJ. The conductivity of compressed powders. A review. Journal of Power Sources. 1978;3:117-136
- [7] Edge M, Hayes M, Mohammadian M, Allen NS, Jewitt T, Brems K, et al. Aspects of poly(ethylene terephthalate) degradation for archival life and environmental degradation. Polymer Degradation and Stability. 1991;2:131-153
- [8] Gupta AK, Chand N, Mansingh A. Anisotropy of dielectric relaxation in poly(ethylene terephthalate) fibres. Polymer. 1979;20:875-878
- [9] Amborski LE. Structural dependence of the electrical conductivity of polyethylene terephthalate. Journal of Polymer Science Part A: Polymer Chemistry. 1962;62:331-346

- [10] Morton WE, Hearle JWS. Physical Properties of Textile Fibres. 4th ed. Manchester, London: The Textile Institute; 1962. pp. 457-484
- [11] Wu CS. Preparation and characterization of an aromatic polyester/polyaniline composite and its improved counterpart. eXPRESS Polymer Letters. 2012;6:465-475
- [12] Urbaniak-Domagała W, Skrzetuska E, Komorowska M, Krucińska I. Development trends in electronics printed: Intelligent textiles produced with the use of printing techniques on textile substrates. In: Ilgu Y, editor. Printed Electronics—Current Trends and Applications. InTech; September 28, 2016. Chapter 7
- [13] Skrzetuska E, Urbaniak-Domagała W, Lipp-Symonowicz B, Krucińska I. Giving functional properties to fabrics containing polyester fibres from poly (ethylene terephthalate) with the printing method. In: Saleh HEM, editor. Polyester. InTech; September 9, 2012. ISBN 978-953-51-0770-5
- [14] Matsuoka M. Nonohmic properties of zinc oxide ceramics. Japanese Journal of Applied Physics. 1971;10:736-746
- [15] Sinclair DC, Adams TB, Morrison FD, West AR. CaCu₃Ti₄O₁₂: One-step internal barrier layer capacitor. Applied Physics Letters. 2002;80:2153-2155
- [16] Chung SY, Kim ID, Kang SJ. Strong nonlinear current-voltage behaviour in perovskitederivative calcium copper titanate. Nature Materials. 2004;3:774-778
- [17] Blatter G, Greuter F. Carrier transport through grain boundaries in semiconductors. Physical Review B. 1986;33:3952-3966
- [18] Tang Z, Huang Y, Wu K, Li J. Significantly enhanced breakdown field in Ca_{1-x}Sr_xCu₃Ti₄O₁₂ ceramics by tailoring donor densities. Journal of the European Ceramic Society. 2018;38: 1569-1575
- [19] Li J, Jia R, Hou L, Gao L, Wu K, Li S. The dimensional effect of dielectric performance in CaCu₃Ti₄O₁₂ ceramics: Role of grain boundary. Journal of Alloys and Compounds. 2015;644:824-829
- [20] Li ST, Li JY, Alim MA. Structural origin of dimensional effect in ZnO varistors. Journal of Electroceramics. 2003;11:119-124
- [21] Skocik P, Neumann P. Measurement of complex permittivity in free space. Procedia Engineering. 2015;100:100-104
- [22] Mohan RR, Mridula S, Mohanan P. Study and analysis of dielectric behavior of fertilized soil at microwave frequency. European Journal of Engineering and Technology. 2015;2:73-79
- [23] Nelson SO. Measurement of microwave dielectric properties of particulate materials. Journal of Food Engineering. 1994;21:365-384
- [24] Scheller M, Koch M. Terahertz quasi time domain spectroscopy. Optics Express. 2009; 17:17723

- [25] Morikawa O, Tonouchi M, Hangyo M. Sub-THz spectroscopic system using a multimode laser diode and photoconductive antenna. Applied Physics Letters. 1999;75:3772
- [26] Jurado A, Escot D, Poyatos D, Montiel I. Application of artificial neural networks to complex dielectric constant estimation from free-space measurements. In: Methods and Models in Artificial and Natural Computation. Santiago de Compostela, Spain: Springer; 2009. pp. 517-526

Properties of Porous Compacts, Polyesters and Ceramics

Electrical Resistivity of Powdered Porous Compacts

Juan Manuel Montes, Francisco Gómez Cuevas, Jesús Cintas, Fátima Ternero and Eduardo Sánchez Caballero

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.76159

Abstract

In this chapter, the problem of the electrical conduction in powdered systems is analyzed. New equations for computing the effective electrical resistivity of metallic powder aggregates and sintered compacts are proposed. In both cases, the effective electrical resistivity is a function of the bulk material resistivity, the sample porosity and the tap porosity of the starting powder. Additional parameters are required to describe the case of non-sintered powder aggregates: one of them describes a certain residual resistivity and another describes the rate of mechanical descaling during compression of the oxide layers covering the particles. Laws for the thermal dependence of these two parameters are also suggested. These new equations modeling the effective electrical resistivity are valid in all the physical range of porosity: from zero porosity to the tap porosity. Links between the proposed equations and the percolation conduction theory are stated. The proposed equations have been experimentally validated with powder aggregates (both in asreceived state and after electrical activation to eliminate oxide layers) and sintered compacts of different metallic powders, resulting in a very good agreement with theoretical predictions. In addition to their general interest, the proposed models can be of great interest in modeling electrical consolidation techniques.

Keywords: electrical resistivity, powder metallurgy, modeling, effective properties, electrical consolidation techniques, FAST

1. Introduction

The theoretical prediction of the effective (or apparent) properties of heterogeneous materials (including multiphase materials, composites, porous materials, etc.) has a remarkable history, on times stimulating the interest of some eminent scientists, including Maxwell, Rayleigh and

IntechOpen

© 2018 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Einstein, among others. In 1873, Maxwell derived an expression for the effective resistivity of a dispersion of spheres within a different material, although only accurate for dilute sphere concentration [1]. In 1892, Rayleigh developed a method to calculate the effective resistivity of an otherwise uniform material interrupted by a rectangular arrangement of spheres of different nature, which is still useful today [2]. In 1906, Einstein determined the effective viscosity of a diluted suspension of spheres, in a work which began the way to model the effective properties of heterogeneous materials [3]. From those first works until today, there has been an upsurge in the number of works dealing with this subject, not only because of the extraordinary intellectual challenge that they represent but also because of their undoubted technological interest.

Porous materials are a good example of heterogeneous materials of technological interest, and we will focus this work on them. Porous materials can be considered as two-phase materials: a phase consisting of the bulk material (fully dense material) and the other constituted by pores.

But, how to model the properties of heterogeneous materials? It is tempting to use 'mixture rules', with the appropriate weighting factors. In the case of porous materials, these rules result in particularly simple expressions, since the properties of one of the phases (the pores) are usually zero. In this way, in order to know the effective properties of porous materials, it would be sufficient to know the properties of the bulk material and the degree of porosity of the sample under consideration. However, for some properties, especially those related to transport phenomena, the aforementioned approach is not sufficient; other factors such as the average size of the pores, their size distribution, etc. are particularly important.

Even the indicated details are not sufficient when the porous materials are made of metallic powders (i.e. the powder metallurgy field). If this is the case, other details must be considered: the material may be the result of cold compacting a mass of powders or the result of compacting and then sintering in a furnace. There are more than mechanical differences between these two situations. From an electrical point of view, for example, in the first situation, metal–metal contacts between particles are not guaranteed. However, in the second case, the sintering process guarantees the electrical continuity (metal–metal contacts) in all the particle junctions. For this reason, the designation of 'porous materials' is too ambiguous. However, with 'powdered porous compacts', we refer to compacted powder aggregates or sintered compacts. Other authors prefer the expression 'granular materials' to refer to the same idea.

Regarding sintered materials, some expressions proposed for generic porous materials may be applicable. **Table 1** shows some of the reported expressions to model the effective electrical resistivity of porous media, obtained by theoretical, empirical or semiempirical means. The expressions in **Table 1** refer to relative (or normalized) resistivity, i.e. the ratio between the effective resistivity of the porous material and the resistivity of the bulk material ($\rho_R = \rho_E / \rho_0$). Some of them were proposed to describe thermal resistivity, but the problem is quite similar (although the transport mechanisms are not exactly the same.)

As can be seen in **Table 1**, most expressions include an empirical parameter. Resistivity is closely dependent on the microstructure (including pore shape and size), and this empirical parameter helps to model the effect of these details. Therefore, a simple mathematical expression based solely on the porosity degree, without any additional empirical parameter, can never accurately describe the electrical resistivity.

Authors	Year	Relative resistivity ($\rho_R = \rho_E / \rho_0$)	Upper boundary condition $ ho_R ightarrow 1$	Lower boundary condition $ ho_R ightarrow \infty$
Maxwell [1]	1873	$\frac{2+\Theta}{2(1-\Theta)}$	$\Theta ightarrow 0$	$\Theta \to 1$
Fricke [4]	1924	$rac{1+c_1\Theta}{1-\Theta}$	$\Theta ightarrow 0$	$\Theta ightarrow 1$
Loeb [5]	1954	$(1-c_2\Theta)^{-1}$	$\Theta ightarrow 0$	$\Theta ightarrow 1/c_2$
Murabayashi et al. [6]	1969	$\tfrac{2+\Theta}{3(1-\Theta)^{c_3}-(1-\Theta)}$	$\Theta ightarrow 0$	$\Theta \to 1$
Aivazov et al. [7]	1971	$\frac{1+c_4\Theta^2}{1-\Theta}$	$\Theta ightarrow 0$	$\Theta ightarrow 1$
Meyer [8]	1972	$\frac{c_5+\Theta}{c_5(1-\Theta)}$	$\Theta ightarrow 0$	$\Theta ightarrow 1$
Schulz [9]	1981	$(1-\Theta)^{-c_6}$	$\Theta ightarrow 0$	$\Theta \to 1$
McLachlan [10]	1986	$\left(1-\frac{\Theta}{\Theta_c} ight)^{-rac{3}{2}\Theta_c}$	$\Theta ightarrow 0$	$\Theta ightarrow \Theta_c$
Montes et al. [11]	2003	$\left(1-\frac{\Theta}{\Theta_M} ight)^{-2}$	$\Theta ightarrow 0$	$\Theta ightarrow \Theta_M$
Montes et al. [12]	2008	$\left(1-\frac{\Theta}{\Theta_{\mathrm{M}}}\right)^{-u}$	$\Theta ightarrow 0$	$\Theta ightarrow \Theta_M$
		$u = 1 + (1 - \Theta_{\rm M})^{\frac{4}{5}}$		
Montes et al. [13]	2016	$\left(1-\frac{\Theta}{\Theta_M} ight)^{-\frac{3}{2}}$	$\Theta ightarrow 0$	$\Theta ightarrow \Theta_M$

The parameters c_1 to c_6 are material constants, Θ_c is a critical porosity (related to the percolation threshold) and Θ_M is the tap porosity of the starting powder (later described)

Table 1. Several expressions for the relative resistivity as a function of the porosity degree (Θ) .

Naturally, the resistivity must increase with the porosity. The greater the porosity, the smaller the electric flow transfer section and the longer the path it must travel, contouring the pores. Most of the expressions in **Table 1** verify that relative resistivity increases from 1 to infinity as porosity varies from 0 to 1. However, this does not apply to powdered materials, as their maximum porosity is always lower than 1. Only the expressions of Loeb [5], McLachlan [10] and Montes et al. [11–13] take this into account, being even applicable in the range of high porosities.

Regarding powder aggregates under compression, modeling is always more difficult. The electrical resistance of the powder mass logically depends on its porosity, decreasing by increasing pressure. So, the bigger the pressure, the lesser is the porosity and therefore the lower is the electrical resistance. But pressure not only helps to reduce the porosity but also, due to the friction between particles, can force the descaling of the dielectric layers (mainly oxides but also hydrides and other chemical compounds) that normally cover the powder metallic particles. Both phenomena lead to decrease the effective resistivity of the powder mass by increasing pressure. These oxides have a high influence on the apparent value of the electrical resistance, to the point that may have more influence than the porosity itself. The influence of oxide layers (with a dielectric behavior) is crucial, since, despite their small thickness, they dramatically influence the conduction process. Some interesting experimental studies, focused on the electrical behavior, have helped to identify the complexity of the phenomena involved [14–16]. Some theoretical studies carried out by Montes et al. [13] have

attempted to identify the most relevant parameters of the problem, ensuring the applicability of the proposed expressions throughout the physical range of porosity and trying to maintain a minimum level of mathematical complexity. The proposed models incorporate parameters as the porosity of the sample, the initial porosity of the starting powder (tap porosity), the resistivity of the metal and the thickness and resistivity of the oxide layers. However, the models also need to incorporate two empirical parameters to describe the mechanical descaling of the oxide layers during the compaction process.

In this chapter, two new models to compute the effective electrical resistivity of metal powder systems under pressure (constituted by oxide-free metallic particles or by oxide-coated metallic particles) will be developed. These models can be considered valid for describing the electrical behavior both of sintered compacts and of powder aggregates, which will be tested to validate the proposed models. The new expressions will be useful to model the electrical consolidation techniques of metallic powders, which are commonly known as field-assisted sintering techniques (FAST).

2. Modeling of the effective resistivity

2.1. Effective areas and effective paths

Let us consider two cylindrical samples of the same material and equal dimensions, the first one being completely solid and the second one with a porosity Θ , as illustrated in **Figure 1**.

As a consequence of the porosity, the electrical resistance cannot be the same in the second sample. The electrical resistance (R) of a bulk material can be calculated from its resistivity. So, for a specimen with nominal section S_N and uniform nominal height of length L_N , the electrical resistance is

$$R = \rho_0 \frac{L_N}{S_N} \tag{1}$$

with ρ_0 being the resistivity of the bulk material.



Figure 1. Diametrical cross sections of two cylindrical samples. Obviously, in the porous material, the electric flow path will be longer and more tortuous, while the transfer cross section will be smaller.

For the porous specimen, which may be produced by uniaxial press and sintering of metallic oxide-free powders, the resistance R' (higher than the one of the bulk specimen) can be calculated in two different ways. On the one hand, it may be considered that the porous material behaves as having an effective electrical resistivity, $\rho_{E'}$ upper than $\rho_{0'}$ and this is

$$R' = \rho_E \frac{L_N}{S_N} \tag{2}$$

On the other hand, assuming that the resistivity of the porous material is equal to ρ_0 , the effective section for the electrical flow to pass, as well as the path length that the flow has to travel, must be different. Being S_E and L_E the effective values of, respectively, the mean transfer section (smaller than the nominal) and mean effective path (longer than the one corresponding to a bulk specimen), the resistance of the porous specimen could be expressed as

$$R' = \rho_0 \frac{L_E}{S_E} \tag{3}$$

It is possible to express S_E and L_E as functions of the specimen porosity (Θ). Thus, by equalling Eq. (2) and Eq. (3), it would be possible to obtain an expression for the effective resistivity, ρ_E , as a function of ρ_0 and the porosity degree. The problem is knowing how the effective magnitudes, S_E and L_E , depend on the porosity. A simple reasoning provides the solution. Let us assume that the porosity of the second specimen in **Figure 1** is completely removed by concentrating the material toward the inside, by decreasing its diameter, as is illustrated in **Figure 2**. The result will be a new, fully dense cylinder of the same height (L_N), cross-sectional area S_E and volume $V_{fully dense} = S_E \cdot L_N$.

According to the definition of porosity

$$\Theta = \frac{V_{void}}{V_{total}} = \frac{V_N - V_{fully \ dense}}{V_N} = 1 - \frac{V_{fully \ dense}}{V_N} = 1 - \frac{S_E \cdot L_N}{S_N \cdot L_N} = 1 - \frac{S_E}{S_N}$$
(4)

and therefore



Figure 2. Initial porous sample and final sample obtained by concentrating all the material and preserving the same nominal height.

$$S_E = S_N (1 - \Theta) \tag{5}$$

This expression is well known in *stereology* and widely used in *quantitative metallography*. As can be checked, $S_E \rightarrow S_N$ as $\Theta \rightarrow 0$ (fully dense material) and $S_E \rightarrow 0$ as $\Theta \rightarrow 1$.

In order to model the mean effective path through a porous specimen, i.e. the distance to travel, eluding pores, from the top to the bottom of the cylinder, a similar expression can be stated. However, two considerations have to be taken into account: (i) we are now dealing with a distance instead of an area; therefore, the factor depending on the porosity should be $(1 - \Theta)^{\frac{1}{2}}$, and (ii) the other way round as with the effective area, the effective length increases with the porosity, and, thus, the relationship should be now inversely proportional.

It is then proposed as follows:

$$L_E = L_N (1 - \Theta)^{-\frac{1}{2}}$$
(6)

As can be checked, $L_E \to L_N$ as $\Theta \to 0$, but $L_E \to \infty$ as $\Theta \to 1$, being equivalent to say that there is not a continuous path.

However, for the description of powdered systems, the previous expressions of S_E and L_E require to be revised. There are also two situations to be distinguished: powder systems with oxide-free particles and powder systems with oxide-coated particles.

2.2. Resistivity of powder systems consisting of oxide-free particles

Until now, we have assumed the porosity to be uniformly distributed and to range from 0 to 1. We shall refer to systems fulfilling these two conditions as *foamed* porous systems, although the limit of $\Theta = 1$ could actually never be reached. The case of systems obtained from powders is far from fulfilling the above-mentioned limits. Theoretically, a sintered compact can be expected to reach a zero porosity upon sintering. However, the upper limit of porosity will never be reached. The maximum porosity in those systems, Θ_{M_r} is the maximum undistorted equilibrium porosity. Essentially, this porosity is equivalent to the tap porosity, i.e. the porosity of a powder mass after being vibrated [17]. This latter parameter describes the pore structure and is very dependent on particle shape, size and distribution, in some way agglutinating morphometric information about the powder. We shall refer to systems satisfying this description as *powdered porous systems*. This entails altering Eq. (5) and Eq. (6) in order to include this upper bound for porosity. The required change is fairly simple and involves replacing the *porosity* (Θ) with the *normalized* or *relative porosity* ($\Theta_R = \Theta/\Theta_M$). Thus

$$S_E = S_N (1 - \Theta/\Theta_M) \tag{7}$$

Now, $S_E \rightarrow S_N$ as $\Theta \rightarrow 0$, as in the fully dense material, but in the upper porosity bound, $S_E \rightarrow 0$ as $\Theta \rightarrow \Theta_{M_r}$ situation where interparticle contacts in the powder are points. S_E represents the effective section for the electrical current transfer, and being this section null, the transfer is not possible.

A similar expression can be stated to model the mean effective path. It is then proposed as follows:

$$L_E = L_N (1 - \Theta/\Theta_M)^{-\frac{1}{2}}$$
(8)

As can be checked, $L_E \to L_N$ as $\Theta \to 0$, but $L_E \to \infty$ as $\Theta \to \Theta_M$, being equivalent to say that there is no continuous path in the non-pressed system.

In previous works, Montes et al. proposed the same theoretical expression for the effective transfer section [18–20] but a different expression for the effective path [21]. The difference is not so large and can be absorbed by very small differences in the values of $\Theta_{M_{\nu}}$ which cannot be empirically discerned due to the experimental uncertainty.

By substituting Eq. (7) and Eq. (8) into Eq. (3), the expression below is obtained:

$$R' = \rho_0 \frac{L_N}{S_N} (1 - \Theta/\Theta_M)^{-\frac{3}{2}}$$
(9)

Equalling Eqs. (2) and (9), the next final expression is obtained:

$$\rho_E = \rho_0 (1 - \Theta/\Theta_{\rm M})^{-\frac{3}{2}} \tag{10}$$

Eq. (10) satisfies the expected boundary conditions, $\rho_E \rightarrow \rho_0$ as $\Theta \rightarrow 0$ and $\rho_E \rightarrow \infty$ as $\Theta \rightarrow \Theta_{M'}$ since, in this last situation, interparticle contacts are points.

It is interesting to compare Eq. (10) with the previously proposed expressions (see **Table 1**). As the exponent 2 in [11] resulted to be too high, when fitting the expression to experimental data, authors were forced to introduce a correction in the value of Θ_{M} , moving it away from the experimentally measured value. Regarding the expression proposed in [12], the exponent u takes different values depending on the value of Θ_M . For instance, and considering extreme values, for $\Theta_M = 0.35$, u = 1.71, whereas for $\Theta_M = 0.65$, u = 1.43. Both 1.71 and 1.43 can be approximated to 1.5. This is supported by the experimental uncertainty in the determination of the Θ_M value. Therefore, as compared with the expression derived in [12], the expression now proposed can be seen as a convenient simplification. Eq. (10) was also derived in [13] following a similar but different approach.

2.3. Resistivity of powder systems consisting of oxide-coated particles

An important detail that must be included to model oxidized powder aggregates is the fact that the oxide films coating the particles are altered throughout the compression process. During the early instants of compression, shear occurs along particle contacts because of sliding [22]. As a consequence of this shear, oxide films locally break, allowing the formation of metal–metal electric paths with rather lower electric resistance [14, 15]. This descaling effect that occurs during particle rearrangement is sufficiently important to be taken into account.

In view of Eq. (10), we can propose a similar expression to model the new situation:

$$\rho_E = \rho_{res} (1 - \Theta/\Theta_{\rm M})^{-n} \tag{11}$$

where ρ_{res} is the residual resistivity (higher than or equal to ρ_0) that would remain at $\Theta = 0$, as a consequence of the mechanical descaling process not being completed. Only if the oxide layers descaling during compression is complete, $\rho_{res} = \rho_0$ (actually, this limit value does not correspond to that of the bulk material, because the oxide layers, once removed, remain in the material and, although representing a very small volume fraction, slightly alter the resistivity value). The exponent *n* is a fitting parameter, which describes the descaling rate; if there are no oxide layers, its value would be equal to 3/2, but with their presence it will take higher values.

Thus, for $\Theta \to \Theta_M$

$$\lim_{\Theta \to \Theta_{\rm M}} \rho_E = \rho_{\rm res} \cdot (1-1)^{-n} = \rho_{\rm res} \cdot (\infty) = \infty$$
⁽¹²⁾

On the other hand, in the limit that $\Theta \to 0$

$$\lim_{\Theta \to 0} \rho_E = \rho_{res} \cdot (1-0)^{-n} = \rho_{res}$$
(13)

Comparing Eq. (11) with Eq. (10), it follows that the minimum value of the exponent n must be 3/2. When the oxide dielectric layers are very thick and/or very resistive, the value of the resistivity during the first moments of compaction will be much higher than with bare particles, and the descaling effect will be very pronounced. Then, the exponent n will take values greater than 3/2.

2.4. Percolation theory relationship

Eqs. (10) and (11) are similar to that derived from the percolation theory [23–26]. In fact, a simple algebraic manipulation of Eq. (10) leads to

$$\rho_{E} = \rho_{0} (1 - \Theta/\Theta_{M})^{-\frac{3}{2}} = \rho_{0} \left(\frac{\Theta_{M} - \Theta}{\Theta_{M}}\right)^{-\frac{3}{2}} = \rho_{0} \left(\frac{1 - \Theta - 1 + \Theta_{M}}{\Theta_{M}}\right)^{-\frac{3}{2}}$$
(14)

and, as the term $(1-\Theta)$ coincides with the relative density ϕ , by defining the relative tap density $\phi_c = (1 - \Theta_M)$, it is obtained that

$$\rho_E = \rho_0 \left(\frac{\phi - \phi_c}{1 - \phi_c}\right)^{-\frac{3}{2}} \tag{15}$$

where the denominator is a constant, so it follows that

$$\rho_E \propto \left(\phi - \phi_c\right)^{-\frac{3}{2}} \tag{16}$$

which is what the percolation theory predicts [23–26], if admitted that ϕ_c , obtained from the tap porosity (Θ_M), represents the percolation bound and 3/2 is the percolation exponent.

A similar reasoning can be applied to Eq. (11), leading to the same conclusion.

2.5. Model comparison

It is instructive to compare the theoretical predictions resulting from Eq. (10) and Eq. (11). Two systems will be considered. The first one is a powder mass with bare particles (applicable to sintered compacts or pressed compacts of deoxidized particles). The second one is a powder mass with particles coated by native oxides (oxidized particles). According to the considered equations, the relative electrical resistivity for both powder masses under compression varies with the porosity degree as shown in **Figure 3**.

As shown, the variation by increasing pressure of both curves starts at the same porosity value (the tap porosity), but the shape is not the same, due to the effect of the oxide descaling.

2.6. Influence of temperature

Although the resistivity of metals increases linearly with temperature, the resistivity of oxide layers decreases with temperature and in a more drastic way, which is usually described by means of an exponential law [27]:

$$\rho_x(T) = A_x \exp(E_x/(2k_B T)) \tag{17}$$

where A_x is a pre-exponential factor, E_x is the band-gap energy and k_B is the Boltzmann constant. So, for sufficiently high temperatures $(T \rightarrow \infty)$, the resistivity of the dielectric or semiconductor layers will be significantly reduced. Dielectric breakdown of the layers may also occur. (Note that the expression $E_x/(2k_B)$ must have temperature dimensions.)

Taking into account this expression, it seems sensible to assume a similar behavior for ρ_{res} and the exponent *n* in Eq. (11), which should vary with temperature as follows:



Figure 3. Relative electrical resistivity (ρ_E / ρ_0 or ρ_E / ρ_{res}) vs. porosity for a powder mass of oxide-free particles (solid line) and oxide-coated particles (dashed line). Curves have been computed by considering the arbitrary values $\Theta_M = 0.6$ and n = 7/2.

$$n(T) = \frac{3}{2} \exp(T_n/T) \tag{18}$$

$$\rho_{res}(T) = \rho_0 \exp(T_\rho/T) \tag{19}$$

where T_n and T_ρ are two convenient temperatures related to the corresponding activation energies.

Thus, as $T \to \infty$, $n \to 3/2$, which is the value that the exponent *n* takes for oxide-free particles (see Eq. (10)), i.e. without dielectric layer coatings. Similarly, as $T \to \infty$, $\rho_{res} \to \rho_0$, i.e. the resistivity of the metal, which means that the oxide effect is zero, as if they were not present.

The electrical resistivity values of the oxide films coating the powder particles are difficult to find. The chemical and physical nature of this oxide film cannot be accurately known in most cases. Moreover, the oxide film may contain metal atoms in various oxidation states, and the oxides may be accompanied by some hydroxides. Moreover, thin oxide films covering particles may behave in a rather different way of bulk oxides. The small thickness of the oxide layer alters the resistivity value by diminishing it, according to the Fuchs-Sondheimer law [27]. It is then concluded that it is difficult to know the exact nature and electrical resistivity of the oxide layers. We also ignore the relationship between T_n or T_ρ and E_x .

Fortunately, it is possible to calculate the values of T_n and T_ρ from Eq. (17) and (18), once the values of n and ρ_{res} are known at room temperature. By isolating n and ρ_{res} from the above equations, we obtain

$$T_n = T \cdot \ln(2n/3) \tag{20}$$

$$T_{\rho} = T \cdot \mathrm{Ln}(\rho_{res}/\rho_0) \tag{21}$$

2.7. Connection with the applied pressure

Eqs. (10) and (11) relate the effective electrical resistivity of the powder aggregate to its porosity. Alternately, it would be possible to take into account the relationship between the electrical resistivity and the applied pressure, as has been done by other authors [28]. However, the fact that Eq. (10) and Eq. (11) are formally equal is a great success of the porosity-based description. The pressure-based description appears to have a narrower applicability, because although sintered compacts are in general previously subjected to compression, there is the possibility of obtaining very porous materials (with metal–metal contacts) without applying pressure, due only to the heat effect, as is the case in loose sintering. In such scenario, it is possible to consider a 'pressure' equal to the driving force that causes the decrease of energy per unit of volume (J/m³ is equivalent to Pa), but this interpretation seems somewhat tortuous and impractical. Therefore, the description based on the porosity appears to have a wider applicability than that based on the applied pressure.

There is also a technical reason for preferring a porosity-based description. Although during the determination of the resistivity-porosity curve, it is also possible to record the applied pressure, and the punches (made of electrolytic copper) limit the value of the highest attainable pressure.

However, it is perfectly possible to make a compressibility curve of the powders reaching very high-pressure values, by using hardened steel punches (The compressibility curve collects information of how the porosity (or relative density) of the powder mass varies when it is subjected to an increasing compression.). Thus, the porosity-based description can be supplemented by an analytical description of the compressibility curve of the powder. Once the corresponding compressibility curve is obtained (Θ vs. P_N), it can be fitted by the least squares method to the analytical expression, for example, the one proposed by Secondi [29], which can be expressed in porosity terms as

$$\Theta = \Theta_{\infty} + (\Theta_{\rm M} - \Theta_{\infty}) \exp\left(-(P_N/a)^b\right)$$
(22)

where Θ is the porosity of the powder mass under a compacting pressure P_N . The parameter Θ_M is again the tap porosity of the powder. The other parameters (Θ_{∞} , *a* and *b*) are fitting parameters.

Therefore, on the one hand, Eqs. (10) and (11) relate ρ_E to Θ , and on the other hand, Eq. (21) relates Θ to P_N . Considering both equations, it is possible to relate ρ_E to P_N , which may be helpful for some situations.

3. Experimental validation

3.1. Materials

To validate Eqs. (10) and (11), four powders (three elemental and one alloy) with different nature, granulometry and tap porosity were chosen. The choice was guided by the intention of checking whether the parameter Θ_M used in the models allows for bringing out these differences.

Table 2 lists the commercial designation of each powder, the designation used here, the mean particle size obtained by laser diffraction and the tap porosity (Θ_M) measured according to MPIF Standards [17]. **Figure 4** shows SEM images with the different powders shape.

The absolute error during the measurement of the Θ_M value, as a function of the employed instrument precision, results to be ± 0.01 : a very small value as compared to the measurements. However, the random vibration process during measuring can lead to an increase of the experimental uncertainty. Experimental checks confirm a higher value around ± 0.05 , which is still a relatively small value.

Powder	Designation	Mean size (µm)	Θ_{M} (measured)
AS61 aluminum (Eckart-Werke)	Al	77.0	0.45
89/11 AK bronze (Eckart-Werke)	Bz	57.2	0.43
WPL 200 iron (QMP)	Fe	84.4	0.63
T255 nickel (Inco)	Ni	18.8	0.86

Table 2. Mean particle size and measured tap porosity (Θ_M) of tested powders.



Figure 4. Scanning transmission microscopy (SEM) images of the four powders used for experimental validations. From left to right and top to bottom: Al, Bz, Fe and Ni.

3.2. Effective electrical resistivity of sintered compacts

There are two possible ways to validate Eq. (10). The first way consists in deoxidizing the powders and subjecting them to varying pressures to determine their resistivity, all under an inert atmosphere that guarantees the non-reoxidation of the particles. The second way consists in pressing the as-received powders (oxidized) to different pressures obtaining different compacts and, once compacted, carrying out a sintering process. This ensures that there are true metal–metal contacts between the particles. Due to the technical difficulties in the first option, the second one has been followed in this work.

Electrical resistance measurements were carried out by using a four-point probe and a Kelvin bridge (micro-ohmmeter), by performing two measurements with inverted polarities to minimize the parasitic effects. The electrical resistance was measured on cylindrical sintered compacts with different porosities. Resistivity was determined from the measured resistance value,

 $R_{m\nu}$ by applying the known expression $\rho_E = 2\pi s R_{m\nu}$ where s = 2 mm, is the distance between the probe electrodes.

These cylindrical samples (about 10 mm height, 12 mm diameter) were prepared by uniaxial cold compaction and subsequent sintering. Several compacting pressures were selected according to the compressibility curve to achieve the desired porosities, which ranged from the maximum allowing a handily specimen to the one obtained for a pressure of 1400 MPa. Afterwards, sintering was carried out for 30 minutes at the temperature indicated in **Table 3** under $1.2 \cdot 10^5$ Pa argon atmosphere. The final porosity after sintering (Θ) was again measured by weighting and measuring the specimens, and the resulting values, shown in **Table 3**, were used in the later calculations.

For comparison purposes, fully dense reference samples of each powder were produced by a double pressing at 1400 MPa (with intermediate annealing to a half of the sintering temperature) and final sintering during 3 hours. **Table 4** gathers the experimentally determined resistivity values of the fully dense samples, used like ρ_0 values. Also, included are the values of the bulk materials, at the measuring temperature (~25°C), found in the literature [30]. These later values are some lower, probably due to the presence in the fully dense samples of some residual porosity and the contamination introduced by the surface oxides of the powder particles.

The *porosity-effective resistivity* data cloud was then fitted to the expression of Eq. (10) by the least squares method. The only fitting parameter was Θ_M . The validity of the proposed model will be assessed depending on how the fitted Θ_M value compares to the experimental value gathered in **Table 2**.

Powder	Sintering temperature (°C)	Porosity range
Al	650	0.01–0.32
Bz	850	0.05–0.10
Fe	1150	0.02–0.43
Ni	800	0.05–0.19

Table 3. Sintering temperature used to produce the tested specimens, previously pressed at different pressures, and porosity range attained.

Powder	Fully dense resistivity ($ ho_0$ [Ω ·m])	Bulk material resistivity ($\Omega \cdot m$)
Al	2.922×10^{-8}	$2.730 imes 10^{-8}$
Bz	1.862×10^{-7}	1.805×10^{-7}
Fe	1.177×10^{-7}	1.043×10^{-7}
Ni	8.197×10^{-8}	6.993×10^{-8}

Table 4. Electrical resistivity of fully dense parts and bulk materials, at room temperature.

Figure 5 shows the data clouds referred to the pairs (Θ , ρ_E) and (Θ_R , ρ_R) for each one of the tested powders. Also shown are the fitted theoretical curves, according to Eq. (10), which is only one when using relative variables. **Table 5** gathers the resulting values of Θ_M after fitting and the coefficients of determination, R^2 , obtained for each one of the powders.

As can be seen, the resulting fitting indicators are quite acceptable. Fitted Θ_M values are inside the accepted uncertainty range of ± 0.05 of the experimental values, except for the Ni powder. In this case, the fitted value (0.71) is far from the experimental one (0.86). This deviation could be due to the filamentary morphology of this powder and its great tendency to form agglomerates. This can distort the measurement of the tap porosity to a value higher than the actual value. A very small compression is sufficient for the porosity to decrease drastically to a value of about 0.7, which is the resultant value of the fitting process. Nevertheless, it seems that for this type of powder morphologies, the tap porosity does not result an adequate parameter.

It is interesting to compare the expression proposed in this chapter with the expressions suggested by other authors (**Table 1**). For this purpose, the experimental curve of the arbitrarily



Figure 5. Experimental results (symbols) and fitted curves (lines) according to Eq. (10). (a) Effective electrical resistivity vs. porosity and (b) relative electrical resistivity (ρ_E/ρ_0) vs. relative porosity (Θ/Θ_M), for the different studied compacts. The vertical lines in (a) represent the fitted Θ_M values of the tested powders.

Θ_{M} (measured)	Θ_{M} (fitted)	R^2
0.45	0.424	0.957
0.43	0.422	0.855
0.63	0.678	0.982
0.86	0.706	0.962
	Θ_M (measured) 0.45 0.43 0.63 0.86	Θ _M (measured) Θ _M (fitted) 0.45 0.424 0.43 0.422 0.63 0.678 0.86 0.706

Table 5. Values of the adjustable parameter of Eq. (10), the tap porosity Θ_M and the resulting coefficients of determination after fitting to the experimental data.
chosen Fe compacts has been fitted with all the expressions (**Figure 6**). The value of ρ_0 has always been set equal to the value shown in **Table 4**, for the fully dense sample.

As can be seen, the expression proposed in this chapter offers one of the best coefficients of determination. For the first seven expressions, the fitting parameter does not have a clear physical meaning, so, nothing can be discussed in favor or against the obtained value. For the McLachlan expression [10], the obtained parameter c results are too low to be identified with the tap porosity. Similarly, for the expression reported by Montes et al. [11], c results are too high, even higher than the measured tap porosity. If the fitting process is forced in these two cases to make the parameter c to move in into admissible values (between 0.58 and 0.68), the coefficient of determination decreases to 0.8960 and 0.7647, respectively. Regarding the expression in [12], the obtained result is quite good, with a realistic value of the fitting parameter, and also with the expression proposed in this chapter, with the added advantage of a being a simpler expression.



Figure 6. Curves resulting after fitting the experimental data of the Fe compacts with the different theoretical expressions gathered in **Table 1**. The value of ρ_0 was fixed to $1.177 \times 10^{-7} \Omega \cdot m$, corresponding to the fully dense sample. The inserted table shows the coefficient of determination and the fitting parameter, *c*, in each expression.

3.3. Effective electrical resistivity of powder aggregates

It is now the intention to validate Eq. (11) for oxidized powder aggregates. The measuring system consisted of a cylindrical die made of alumina (12 mm inner diameter and resistivity ~10¹² Ω ·m), with an external steel hoop to reinforce the brittle ceramic. Two electrodes (of electrolytic copper) closed the die, with the powder mass in the middle. The porosity of the powders was reduced by increasing the pressure and therefore moving the upper electrode (the lower one remained fixed). After pouring the powder into the die, it was vibrated according to the standards [17] in order to reach the tap porosity. The measuring process started soon after the upper punch touched the powders. At each step, the height of the powder column and its electrical resistance were recorded (the former through the displacement of the universal testing machine frame, and the latter through a micro- or kilo-ohmmeter connected to the electrodes). The load was increased to record a new point. For each measured resistance value (*R*), the effective resistivity value (ρ_E) can be calculated using the well-known formula $\rho_E = R \cdot S/H$, where *S* is the cross-sectional area and *H* is the height of the powder column. The porosity can also be easily computed from the powder column height.

The experimental results and fitted theoretical curves according to Eq. (11) are shown in **Figure 7**. Note that although for the representation in **Figure 7b** relative variables have been used, there is not a common theoretical equation for all the powders because the influence of the descaling process is different from each one. Fitted values of the adjustable parameters (Θ_{M} , ρ_{res} and *n*), as well as the coefficients of determination, R^2 , are gathered in **Table 6**. As can be seen, the results are quite consistent, with coefficients always greater than 0.99.

Now, in all cases, fitted Θ_M values are within the experimental uncertainty (about ± 0.05). The obtained value for Ni is interesting, now in a total agreement with the measured value despite the morphological characteristics of the powder have not changed. The presence of two other fitting parameters allows Θ_M reaching the objective value, which probably causes a slight



Figure 7. Experimental results (symbols) and fitted curves (lines) with Eq. (11) of (a) the effective electrical resistivity vs. porosity and (b) relative electrical resistivity (ρ_E/ρ_{res} , with ρ_{res} taken from **Table 6**) vs. relative porosity (Θ/Θ_M), for the four studied powders. The vertical lines in (a) represent the fitted tap porosity values.

Powder	Θ_{M} (fitted)	$ ho_{res}$	n	<i>R</i> ²	Θ_{M} (measured)	$ρ_x$ (Ω·m)
Al	0.436	1.618×10^{-5}	2.311	0.990	0.45	$1.0 imes 10^{12}$ [31]
Bz	0.446	$1.880 imes 10^{-7}$	3.639	0.987	0.43	$1.0 imes 10^2$ [32]
Fe	0.673	2.263×10^{-6}	3.200	0.998	0.63	$2.1\times10^3[33]$
Ni	0.860	1.000×10^{-6}	1.522	0.998	0.86	$8.0 imes 10^2$ [34]

For comparison purposes, in the last two columns, the measured value of Θ_M and the oxide resistivity at room temperature, found in thin film-specialized literature, are shown

Table 6. Fitting parameter values and coefficient of determination for the studied powders.

alteration in the other parameters. Unfortunately, the filamentary morphology of the powder does not allow to be totally confident with the obtained results.

A detailed study of the fitted value of ρ_{res} and *n* is also worth performing. Regarding the value of ρ_{resr} and also considering the ρ_x value shown in **Table 6**, it can be said that there is a correlation between the two values: if the values of ρ_{res} and ρ_x are ranked from highest to lowest, the list obtained is the same. This is logical, considering that ρ_{res} is due to the remains of the oxide layers that have not been removed.

Obviously, the values of ρ_{res} cannot be lower than those of the bulk metal, ρ_{0r} given in **Table 4**. As can be seen, all the values of ρ_{res} exceed in one or more orders of magnitude of the corresponding values of ρ_{0r} with the exception of the bronze (Bz) whose ρ_{res} is only slightly higher than its respective value of ρ_0 . This very small difference means that the oxide can flake out completely or that the oxide layer is much thinner in this powder.

On the other hand, the results obtained for *n* are not so easy to interpret. Obviously, these have to do with the oxide descaling easiness. But the nature of this phenomenon is complex, depending on multiple factors: the shape, size and hardness of the particles, the thickness of the oxide layers, the mechanical strength and brittleness of these layers, etc. The difficultness to collect all this information aggravates the problem [35].

It is possible, however, as already mentioned, to calculate the values of the activation energies associated with the parameters *n* and ρ_{res} , present in Eq. (11). **Table 7** shows the resulting values after replacing in Eq. (19) and Eq. (20) in the values of *n* and ρ_{res} shown in **Table 6** for tests carried out at room temperature (298 K).

Powder	<i>T_n</i> (K)	$T_{ ho}$ (K)
Al	128.846	$1.88 imes 10^3$
Bz	264.095	2.87
Fe	225.792	$8.81 imes 10^2$
Ni	4.334	$7.45 imes 10^2$

Table 7. Activation energies associated with parameters *n* and ρ_{res} .

The relatively small differences in the *n* and ρ_{res} values shown in **Table 6** are now magnified. A clear difference is found among resulting values. Concerning T_n , the Ni powder shows a value of two orders of magnitude lower. This means that for temperatures not too high, the effect of the nickel oxide will not be much important. In the limit situation, with oxide-free particles, T_n takes the limit value 0 at any temperature. When the oxide is present, the value of T_n gives an idea of the effect of the oxide at the considered temperature. On the other hand, according to the T_ρ values, for temperatures not too high, the resistivity of the bronze oxide will be similar to that of the metal. The effect of the resistivity at different temperatures can be followed with the T_p value.

3.4. Model application

Up to now, the goodness of the developed relationships between electrical resistivity and porosity has been checked, both in oxide-free and oxide-covered particles. As a result, the fitting parameters of the model have been proven to agree with the expected ones or, in some cases, have just been determined to fit the experimental data. A step further in the applicability of the final model (considering the previously obtained fitting parameters) consists in comparing the predictions for new situations with the corresponding new experimental results, this time without free value parameters.

However, before undertaking this, there is still a pending issue, defining the relationship between ρ_E and P_N stablished in Eq. (21). The first step consists in subjecting the selected powders to compression tests, using a universal testing machine according to the standards [36]. **Figure 8** shows the obtained curves (in Θ vs. P_N representation) and the theoretical curves resulting from fitting by the least squares method the experimental curves to the Secondi expression. **Table 8** gathers the values of the parameters involved in Eq. (21) and the obtained determination coefficients.

There are not many comments to make about the results, because apart from Θ_{M} , the other parameters do not have a physical meaning. Regarding Θ_{M} , the fitted values are inside the uncertainty interval except for the Ni powder. In this case, the fitted value is again quite different to the experimentally measured, but being the same as the one obtained when also working with oxide-covered powders during checking of Eq. (11). The powder morphology accounts again for the observed difference.

Once the values of the parameters present in Eq. (10) and (21) are known, the predictability of the model can be checked. For this purpose, new electrical resistance measurements were made on the four powders under some different experimental conditions. An 8-mm-internal diameter die was used (instead of the one used to determine compressibility and compressibility/resistivity curves, with 12 mm). Measurements were made with three different masses, 6, 8 and 12 g and with four different pressures (25, 50, 75 and 100 MPa). The measured values of electrical resistance and the predicted values obtained using Eq. (10), Eq. (21) and the known expression $R = \rho_E H/S$ are shown in **Figure 9**, for the iron powder. As can be seen, the values differed by less than 2%, with an average relative error of 0.83%, which can be considered a reasonable agreement. For the remaining powders, similar results were obtained.



Figure 8. Experimental compressibility curves and corresponding fitted curves obtained by fitting by the least squares method the Secondi expression to the experimental data.

Powder	Θ	Θ_{M}	а	b	R^2
Al	0.007	0.494	110.6680	0.8381	0.9998
Bz	0.000	0.430	759.5506	0.7865	0.9923
Fe	0.016	0.645	304.9329	0.7967	0.9997
Ni	0.130	0.716	329.6176	0.8132	0.9997

Table 8. Fitted values of the parameters involved in the Secondi expression (Eq. (21)).

3.5. Electrical activation

In some electrical consolidation techniques of powders, it is practical to incorporate an electrical activation stage, whose purpose is precisely to eliminate the insulating effect of the oxide layers by electrical means. It is possible to avoid the effect of these oxide layers by employing high or medium voltages (>200 V). High electrical currents are not necessary. During the first moments of the process, the interparticle contact areas are very small and therefore very resistive, and the local temperature of these areas can quickly and notably increase. This local



Figure 9. Measured and predicted resistance values for Fe powder columns under different pressures and masses.

temperature increment will result in a drastic decrease in the resistivity of the oxide layers, dielectric or semiconductor in nature. If the local temperature or applied electric fields become sufficiently high, the dielectric breakdown of these layers could also occur, often leading to an irreversible degradation.

In order to test both the model and the efficiency of the electrical activation process, the resistance measurements obtained after activating Fe powder columns (under the same aforementioned conditions), and the predicted values through the model of oxide-free particles given by Eq. (10), are compared. The electrical discharge came from an autotransformer capable of providing a voltage of 0–220 V and a maximum current of 10 A, protected by a magnetothermic circuit breaker. The voltage was slowly increased until the circuit breaker opened the circuit. Then, resistance measurements were carried out. **Figure 10** shows the measured electrical resistance values, as well as the predicted ones. In this case, the maximum relative error is 9.5%, with seven of the experiments having an error greater than 5%, and with an average relative error of 4.9%.

It is worth noting that the resistance values shown in **Figure 9** are three orders of magnitude higher than those shown in **Figure 10**. The higher values must be due to the presence of oxide layers, only partially peeled by pressure, and to their absence (partial or total) in the second case. After the application of the electrical activation, resistivity decreases as a consequence of the temperature increase or the degradation of the dielectric layers. The observed differences between experimental and theoretical values suggest, however, that the invalidation effect of the oxide layers is not complete. Certainly, the activation process also has a strongly erratic component forming randomly privileged electrical pathways, thus making the process non-uniform and deviating from the proposed model. Despite these differences, and according to the measured and predicted values shown in **Figures 9** and **10**, it can be concluded that the model can be considered satisfactorily validated.



Figure 10. Measured and predicted resistance values for Fe powder columns under different pressures and masses and with a previous activation stage.

4. Conclusions

Two new equations to calculate the effective electrical resistivity of metal powder systems under pressure (constituted by oxide-free or oxide-coated metallic particles) have been developed. According to these equations, the effective electrical resistivity can be expressed as a function of the material resistivity, the porosity degree of the sample and the tap porosity of the starting powders. The latter parameter is considered a fitting parameter in the model, to be determined with initial experiences. To model powder aggregates of oxide-coated particles, two fitting parameters describing the powder descaling phenomenon are also necessary: the residual resistivity and the exponent value. This descaling phenomenon must be considered in the model to explain that resistivity does not tend to the bulk metal value if extrapolated to zero porosity and to justify the greater rate of reduction in resistivity by decreasing porosity (as compared to the case of oxide-free particles). However, both equations are formally similar from a mathematical point of view.

The validity of these equations has been experimentally tested, using sintered compacts (similar to oxide-free powder system) and powder aggregates (similar to oxide-coated powder system) of aluminum, bronze, iron and nickel with different porosity degrees. The agreement between experimental and fitted theoretical values is quite good.

The proposed equations are suitable to describe the early stages of electrical consolidation techniques. The efficiency of the electrical activation process (which causes the dielectric breakdown of the oxide layers) has been tested and interpreted on the basis of the equations presented here. The results obtained confirm the goodness of the proposed models.

Acknowledgements

Financial support of the Ministerio de Economía, Industria y Competitividad (Spain) and Feder (EU) through the research projects DPI2015-69550-C2-1-P and DPI2015-69550-C2-2-P is gratefully acknowledged. The authors also wish to thank the technicians J. Pinto, M. Madrid and M. Sánchez (University of Seville, Spain) for their experimental assistance.

Author details

Juan Manuel Montes¹, Francisco Gómez Cuevas², Jesús Cintas¹, Fátima Ternero¹* and Eduardo Sánchez Caballero¹

*Address all correspondence to: fternero@us.es

1 Metallurgy and Materials Science and Engineering Group, Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Sevilla, Spain

2 Department of Chemical Engineering, Physical Chemistry and Materials Science, Escuela Técnica Superior de Ingeniería, Universidad de Huelva, Huelva, Spain

References

- Maxwell JC. A Treatise on Electricity and Magnetism. New York: Dover Publications Inc.; 1998 (reprinted)
- [2] Rayleigh L. On the influence of obstacles arranged in a rectangular order upon the properties of medium. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science. 1892;34:481-502
- [3] Einstein A. Eine neue Bestimmung der Moleküldimensionen. Annals of Physics. 1906;19: 289-306
- [4] Fricke H. A mathematical treatment of the electric conductivity and capacity of dispersed systems. Physical Review Journals. 1924;24:575-587
- [5] Loeb AL. Thermal conductivity: III, a theory of thermal conductivity of porous materials. Journal of the American Ceramic Society. 1954;37(2):96-99
- [6] Murabayashi M, Takahashi Y, Mukaibo T. Effect of porosity on the thermal conductivity of ThO₂. Journal of Nuclear Science and Technology. 1969;6(11):657-662
- [7] Aivazov MI, Domashnev IA. Influence of porosity on the conductivity of hot-pressed titanium nitride specimens. Poroshkovaya Metallurgiya. 1968;9(69):51-54

- [8] Meyer R. The measurement of electrical resistivity to characterize a sintered product. Powder Metallurgy International. 1972;4(2):63-67
- [9] Schulz B. Thermal conductivity of porous and highly porous materials. High Temperatures-High Pressures. 1981;13:649-660
- [10] McLachlan DS. Equation for the conductivity of metal Insulator mixtures. Journal of Physics C: Solid State Physics. 1986;19:1339-1345
- [11] Montes JM, Rodríguez JA, Herrera EJ. Thermal and electrical conductivities of sintered powder compacts. Powder Metallurgy. 2003;46(3):251-256
- [12] Montes JM, Cuevas FG, Cintas J. Porosity effect on the electrical conductivity of sintered powder compacts. Applied Physics A: Materials Science & Processing. 2008;92:375-380
- [13] Montes JM, Cuevas FG, Cintas J, Gallardo JM. Electrical conductivity of metal powder aggregates and sintered compacts. Journal of Materials Science. 2016;51:822-835
- [14] Garino TJ. Electrical behavior of oxidized metal powders during and after compaction. Journal of Materials Research. 2002;17(10):2691-2697
- [15] Lefebvre LP, Pleizier G, Deslandes Y. Electrical resistivity of green powder compacts. Powder Metallurgy. 2001;44(3):259-266
- [16] Cheng-Feng LI, Shen-Gang ZHU. Apparent electrical conductivity of porous titanium prepared by the powder metallurgy method. Chinese Physics Letters. 2005;22(10):2647-22650
- [17] MPIF. Standard 46, Determination of Tap Density of Metal Powders. Princeton: MPIF; 2002
- [18] Montes JM, Cintas J, Rodríguez JA, Herrera EJ. Effective pressure on powders under uniaxial compression. Journal of Materials Science Letters. 2003;22:1669-1671
- [19] Montes JM, Cuevas FG, Cintas J. A new expression for the effective pressure on powders under compression. Computational Materials Sciences. 2006;36:329-337
- [20] Montes JM, Cuevas FG, Cintas J. Effective area in powder compacts under uniaxial compression. Materials Science and Engineering A. 2005;395:208-213
- [21] Montes JM, Cuevas FG, Cintas J, Rodríguez JA, Herrera EJ. The equivalent simple cubic system in trends. In: Materials Science Research. New York: Nova Publishers; 2005. pp. 157-190
- [22] German RM. Particle Packing Characteristics. Princeton: MPIF; 1989
- [23] Efros AL. Physics and Geometry of Disorder. Percolation Theory. Moscow: MIR; 1985
- [24] Stauffer D, Aharony A. Introduction to Percolation Theory. London: Taylor and Francis; 1994

- [25] Torquato S. Random Heterogeneous Materials: Microstructure and Macroscopic Properties. New York: Springer; 2009
- [26] Sahimi M. Heterogeneous Materials I. New York: Springer; 2003
- [27] Tsuda N, Nasu K, Fujimori A, Siratori K. Electronic Conduction in Oxides. 2nd ed. Berlin: Springer-Verlag; 2000
- [28] Euler KJ. The conductivity of compressed powders. A review. Journal of Power Sources. 1978;3:117-136
- [29] Secondi J. Modeling powder compaction from a pressure-density law to continuum mechanics. Powder Metallurgy. 2002;45(3):213-217
- [30] Brandes EA (editor). Smithells Metals Referente Book (6th edition). United Kingdom: Butterworths; 1983
- [31] Li WT, McKenzie DR, McFall WD, Zhang QCH, Wiszniewski W. Breakdown mechanism of Al₂O₃ based metal-tometal antifuses. Solid State Electronics. 2000;44:1557-1562
- [32] Drobny VF, Pulfrey DL. Properties of reactively-sputtered copper oxide thin films. Thin Solid Films. 1979;61:89-98
- [33] Akl AA. Optical properties of crystalline and non-crystalline iron oxide thin films deposited by spray pyrolysis. Applied Surface Science. 2004;221:319-329
- [34] Guziewicz M, Grochowski J, Borysiewicz M, Kaminska E, Domagala JZ, Rzodkiewicz W, Witkowski BS, Golaszewska1 K, Kruszka R, Ekielski M, Piotrowska A. Electrical and optical properties of NiO films deposited by magnetron sputtering. Optica Applicata. 2011;XLI(2):431-440
- [35] Huntz AM, Andrieux M, Molins R. Relation between the oxidation mechanism of nickel, the microstructure and mechanical resistance of NiO films and the nickel purity. II. Mechanical resistance of NiO films. Materials Science and Engineering: A. 2006;417:8-15
- [36] MPIF. Standard 45, Determination of Compressibility of Metal Powders. Princeton: MPIF; 2002

Chapter 3

Electrical Properties of Polyesters

Wieslawa Urbaniak-Domagala

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.78612

Abstract

Polyesters occupy an important place in the group of polymers as engineering materials to be used in electrotechnology and electronics. These polymers are characterized by excellent electro-insulating properties, showing mechanical strength, thermal resistance, and easiness in processing at the same time. The chapter presents the behavior analysis of the following polyesters in electric field: poly(ethylene terephthalate), poly(lactic acid), and polycarbonate. The effect of polymer microstructure on electric properties is presented, including its susceptibility to polarization that makes it possible to use polyesters as electrets materials. The second trend of the study presents the possibilities of transforming the electro-insulating properties of polyester fabrics to conductive properties with the use of modern processing methods such as PVD, CVD, and digital print. The functionalization of polyester fabrics extends their application range, for example, in e-textiles and reduces the fabric susceptibility to static electricity, increasing the safety of use.

Keywords: polyesters, electrical conductivity, polarization, electrets, static electricity

1. Introduction

Polyesters constitute an important group of polymers widely used in many branches of economy, such as electrical, electronic, building, clothing and packaging industries, and medicine. These polymers are characterized by excellent electro-insulating properties, mechanical strength, thermal resistance, and susceptibility to multiple processing. A common feature of polyesters is the presence of ester group in the main chain structure. This group imparts a polar character to polyesters. Aromatic groups in the repeatable units of polyester chain impart to the polymers an increased physical resistance, such as thermal (increased melting point and glass transition temperature) and mechanical resistance (increased mechanical

IntechOpen

© 2018 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

parameters such as elasticity and strength). The content of aromatic structures in polyesters is different and has been used for the internal classification of these polymers into aliphatic, aliphatic-aromatic, and aromatic polyesters. Aliphatic polyesters contain no aromatic structures, for example, poly(ethylene adipate). This group includes biodegradable polyesters, such as poly(lactic acid) (PLA) (**Figure 1B**), polyesters of butyric acid (PHB), and poly(butylene succinates) (PBS) widely used in medicine and technology. Aliphatic-aromatic polyesters contain both the aliphatic and aromatic structures (e.g., poly(ethylene terephthalate), polycarbonates) (**Figure 1C**, **D**). These polyesters show very good thermo-mechanical, impact, tribological, and optical properties, as well as resistance to atmospheric and functional conditions, which qualify them for mass production and versatile use. Finally, polyesters with "purely" aromatic structures – polyarylates (poly(4-hydroxybenzoate), poly(bishfenol-A-terephthalate), liquid crystal polyester) that show excellent thermal and dimensional stability, impact resistance, fire resistance, and nonlinear optical properties (NLO) [1]. Aromatic polyesters are used in the production of membranes, films coatings for electronic and electrical industries, optical waveguides and devices doubling the frequency of electromagnetic waves [1].

The chapter presents the behavior analysis of the following polyesters in DC electric field: aliphatic-aromatic polyesters with the example of poly(ethylene terephthalate) (PET) and polycarbonate (PC) and aliphatic polyester with the example of poly(lactic acid).

The processes of nonstationary current flow in polyesters and possible mechanisms that generate the nonstationary states are presented. Using the example of PET film tests, the ionic character of current conduction is shown. It is the effect of air humidity in the environment where a product is used that is connected with the ionic character of current conductance. There observed a well-known effect of deteriorating the PET film electro-insulating properties with increasing the content of water vapor in air [2]. In this study, it has been shown that this effect additionally depends on the form of product, and it is particularly intensified in fibrous structures, where the conduction is increased by about 1000 times. The effect of the physicochemical state and coarseness of surface on the level of static electricity charge is shown. The processes of static electricity of polyesters, electricity conditioning, and hypotheses explaining these processes with a particular consideration of the static electricity of polyester-metal contact are discussed. The polyesters are important precursors for making electrets. The various techniques of electrets making and the issues of the electric charge relaxation that are of

a)	b)		$ \underbrace{+ \left(\begin{array}{c} CH_{3} \\ -C \\ -C \\ CH_{3} \end{array} \right) - 0 - 0 - 0 \\ d \right)}_{d} $
Ester group	Aliphatic polyester Polylactide (PLA)	Aliphatic-aromatic polyester, Poly(ethylene terephthalate (PET)	Aliphatic-aromatic polyester Polycarbonate (PC)

Figure 1. Structures of chemical groups in polyesters.

great importance for the electrets stability are presented. Information about the development trends of polyester and new fields of application are also included.

2. Electrical conductance of polyesters in a DC field

Polyesters are real dielectrics with a low electric conductance, polarizability in electric field, and a strong susceptibility to static electricity. Electric properties are determined by the presence of connected charges and trace quantities of free electric charges that are generated by defects, impurities, technological additives, or injected from electrodes or environment (e.g., low-temperature plasma). During the interaction of DC field, free charges undergo migration and connected charges are polarized. Migration and polarization processes occur in parallel, shaping a characteristic, nonstationary image of the polymer electric conductance.

The current that flows in a real polymeric dielectric under DC field is transient in nature and called absorption current. The density of absorption current decreases in time to reach a steady-state value called conductance current. The transient (absorption) current "j(t)" is presented as a sum of the steady-state conduction current " $j_{c,"}$ " the transient current (displacement current) " $j_n(t)$," and diffusion current " j_{d} ":

$$j(t) = j_{c} + j_{d} + j_{v}(t)$$
(1)

In many polymers, the decreasing transient polarization current is in a direct relation with the function of polarization decay P(t). The polarization decay occurs according to the dependence:

$$P(t) = P_o \cdot \exp\left(\frac{t}{\tau_p}\right) \tag{2}$$

where: t – time and τ_p – macroscopic relaxation time of electrical polarization. The decrease in current in dielectric polymer can be approximated by Curie function:

$$j = A \cdot t^{-n} \tag{3}$$

where: A—coefficient of proportionality dependent on temperature, n—power coefficient dependent on relaxation processes, n < 1 for times $t > \tau$, while n > 1 for $t < \tau$. With the use of the above approximation to transient conduction processes in PET, the following values of power coefficient are obtained: n = 0.75 [3], n = 0.33 [4], and n = 0.79 [5]. The transient character of current indicates a complicated behavior of electric charges in dielectric polymers. The values of conductance current are lower by one to several orders compared to the initial absorption current and the time of reaching a steady-state value is from several minutes to dozen hours depending on polymer. To metrologically characterize a polymer, it is indispensable to determine the isochronal absorption current (i.e., current at constant times).

Test results indicate that the transient character of current depends on the factors connected with the object tested (chemical structure and the presence of polar groups, physical microstructure, thermal and electric history of a sample) and test conditions (field intensity, temperature and relative humidity of the medium, and electrode material and the presence of residual charge in the material tested).

Das-Gupta in his studies [7–9] has presented several mechanisms explaining the transient current flow in polymers. His intention was to indicate a method of identifying the mechanism type. The identification consists in performing a series of tests for the given polymer: relationship between electric field and the isochronal current transient, temperature dependence, effect of electrode material, thickness dependence, and time dependence of transient current. Then, the test results are analyzed with respect to the probability of the given mechanism. Das-Gupta characterizes the features of five mechanisms potentially generating transient current flows:

- **1.** Electrode polarization: isochronal current proportional to field, a strong effect of the electrode material by blocking the flow, the process is thermally activated, power coefficient: initially n = 0.5 followed by n > 1.
- 2. Orientation of dipoles uniformly arranged through the polymer volume: isochronal current proportional to field, the process is thermally activated, electrode materials and thickness sample independent of isochronal current at DC field, power coefficient $0 \le n \le 2$.
- **3.** Charge injection forming trapped space charge: isochronal current is controlled by injection method (electronic, corona discharge, and glow discharge methods), the thickness sample independent of isochronal current at DC field, dependence electrode material related to injection method, thermally activated process related to injection method, power coefficient $0 \le n \le 1$.
- **4.** Charge tunneling from electrodes to empty traps: (isochronal current proportional to field, thickness sample inversely proportional dependent of isochronal current at DC field, the process is thermally independent, strongly dependence electrode material, power coefficient $0 \le n \le 2$
- 5. Hopping of charge carriers from one localized state to another: isochronal current proportional to field, the process is thermally activated, thickness sample and electrode materials independent of isochronal current at DC field, power coefficient $0 \le n \le 2$.

The starting point of recognizing the conductance process is the determination of charge carrier nature (electrons, ions). The assessment of carrier types is carried out by direct testing through comparing the charge transferred with the mass of substance released on electrodes in contact with the polymer (mass spectrometry and neutron activation analysis). Indirect methods include: tests of voltage-current and current-temperature characteristics [5, 10, 11], dielectric tests [12], tests of photo-electric and electro-chemical effects as well as tests of the dependence of polymer conductance on pressure [13]. The image of the pure polymer conductance significantly differs from that of polymer containing ionogen compounds (e.g., stabilizers, catalyst residues, impurities, other additives, and products of chemical decomposition). Compounds of this type (e.g., water) easily dissociate in volume or on the polymer surface imparting an ionic character to conductance.

In studies carried out on a pure PET, their authors present divided views: Amborski [10], Saito [13] declare themselves in favor of the ionic conductivity mechanism in PET. Based on testing the electro-chemical effect with the use of thermally stimulated currents (TSC), Sawa [14] concludes that electronic conduction occurs at temperatures to Tg and ionic conductance at temperatures above Tg. The concept of ionic conductance in polymers is based on the assumption of the presence of molecules capable of dissociating in the polymer structure and various structural effects that determine the available internal volume of polymer and are responsible for the diffusion processes and ion transport in the polymer volume. The migration of free ions consists in specific, hopping change in ion positions [15] Charge motion is given by the carrier hopping over the potential barrier. It takes place from one to the other position, in which the ion achieves the minimal value of potential energy. The mobility of free ions is limited by the value of potential barrier $W_{B_{p}}$ which should be defeated by the ion during migration. The electric field reduces the barrier by the value " Δ ":

$$\Delta = \frac{1}{2}e \cdot a \cdot E \tag{4}$$

where: E is DC field intensity, e—electron charge, and a—hopping dislocation path of ion. Based on the calculations of the probability of change in ion position in the polymer during migration and the rate of ion dislocation from one to the other position [15], the current density of conduction under the conditions of the DC action can be given as follows:

$$j = z \cdot e \cdot n \cdot \left(a \cdot v \cdot \exp\left[-\frac{W_B}{kT}\right] \cdot 2 \cdot \sinh\left[\frac{z \cdot e \cdot E \cdot a}{2kT}\right] \right) = G \cdot \sinh(H \cdot E)$$
(5)

where: z-number of elementary charges, e-electron charge, n-density of dissociated molecules, a-path of the charge hopping dislocation, k-Boltzmann constant, $W_{\rm B}$ -barrier of the charge potential energy, E-DC field intensity, T-temperature, G and H-constants in the generalized form of Eq. (5).

2.1. Electrical conductivity of poly(ethylene terephthalate) films

Poly(ethylene terephthalate) is a commonly used polymer in electrical engineering and electronics, where its electro-insulating properties are successfully used. In this study, commercial PET films, Estrofol type, containing indispensable additives, such as catalysts and stabilizers: manganese acetate (0.035% by wt.), calcium acetate (0.052% by wt.), antimony trioxide (0.040% by wt.), and phosphorus compounds (0.035% by wt.) were tested. Three variants of PET film with different supermolecular structures were tested: oriented films technologically drawn in a single-axis direction in a ratio of 2×, 3.5×, and 4×.

Al electrodes with a protective ring were evaporated on the purified film surface. The kinetics of absorption/desorption (depolarization) currents were examined for 20 min with the use of the measurement system described in paper [16]. **Figure 2** shows the kinetics of the volume absorption current in PET film (**Table 1**, draw ratio 4.0×) measured for 10 min. After this time, DC field was turned out and with earthed electrodes, the depolarization current (desorption current) was recorded for 10 min.



Figure 2. Decay of the transient (A) and depolarization (D) currents $I_v = f(t)$ in a PET film (R = 4.0×) under a DC field (Al electrodes, t = 23°C, RH = 25%).

Film symbol	Draw ratio	Thickness, μm	Density kg/m ³	Crystallinity degree*, %	Herman's coefficient of orientation, fo
A	2.0x	79	1344	7.4	0.12
B	3.5x	57	1352	14.5	0.44
C	4.0x	54	1358	19.8	0.58

* determined by the densitometric technique.

Table 1. Characteristics of PTE films.

Current-voltage characteristics were determined on the basis of the absorption current corrected by the desorption component according to the procedure of Badiana [17]. The characteristics j = f(E) shown in **Figure 3** indicate linear behavior of the films and a shift into nonlinear state at an intensity of 3.5×10^7 V/m. Based on the nonlinear range of field intensity that in the case of samples B and C is developed within a high range of the intensity of field E, the analysis of the ionic conductance of the films was carried out.

The experimental current-voltage characteristics of samples B and C were approximated with the Eq. (5). The approximation consisted in directing the function: $j = G \cdot \sinh H \cdot E$ to a linear form, that is, to develop it into Taylor series according to the procedure given in monograph [18], taking into account only the linear elements of this solution. In calculations based on the minimization procedure, the following parameter values were obtained:

- for PET (R = 3.5×) G = 7.20 × 10⁻¹³ m/V, H = 2.4×10^{-8} m²/A, a = 1.24 nm
- for PET (R = 4.0×) G = 7.41 × 10⁻¹³ m/V, H = 2.4 × 10⁻⁸ m²/A, a = 1.24 nm
- a-path of the hopping shift of charge between successive equilibrium positions.



Figure 3. Characteristics of PET films. Films denotation according to Table 1.

Parameter "H" characterizes the migration of the charge carriers in the process of conduction. With an assumption of one carrier type (e.g., proton, z = 1), the path of protons in the PET tested amounts to 1.24 nm and is the same for the film stretched 3.5 and 4.0 times. The value calculated is probable if we consider the distances between PET macromolecules. The investigations of PET films by the method of wide-angle diffraction [19] prove that the phenyl ring planes of macromolecules in the crystalline areas are oriented in parallel to the film plane. The distance between the phenyl ring planes perpendicular to the film plane (i.e., toward field E)— thus toward the motion of charge carriers according to the calculation [19], it amounts to 0.32 nm. If the migration of charge carriers occurs in the noncrystalline areas of polymer, where the intermolecular distances are higher than 0.32 nm, the value of the charge hopping shift is real. **Figure 4** shows the comparison of theoretical and experimental j = f (E) characteristics of PET films.

The conformity of current-voltage courses allows one to think that in the PET films tested, the conduction of charges is of ionic character. The resistivity of PET films calculated for the proportional range of characteristics I = f(U) is for R = $2.0 \times \lg \rho_v = 15.400 \pm 0.157$, for R = $3.5 \times \lg \rho_v = 15.500 \pm 0.128$, and for Rx = $4.0 \lg \rho_v = 15.277 \pm 0.177$. It seems that the structural differences in the films tested do not influence the DC conductance in a statistically significant way.

Urbaniak-Domagala has presented in her study [16] the tests results of DC conductance in polylactide film. The tests were carried out with the use of Al and Au rigid electrodes within the range of DC field from 8.3 to 33.3 MV/m. In DC field, polylactide behaves as PET, showing a low conductance, a transient in nature current flow, dependence of current density on the electrode material j _{PET-AL-PET} > j _{PET-Au-PET} and a low energy of the conduction activation energy (0.4–0.7) eV that increases in the area of glass transition (0.9–1.1) eV.



Figure 4. Comparison of theoretical and experimental density current - DC field intensity characteristics of PET films.

2.2. Effect of the medium relative humidity (RH) on the electric conductance of PET products in DC field

There are many examples of end products (films woven and knitted fabrics, nonwovens) designed for protective applications, such as electro-insulating barriers and protective clothing that are used under variable environmental conditions. Environmental factors bring about polymer aging [2]. Qualitative and quantitative tests of the polyester product aging have shown a significant effect of water vapor in air as an ionogenic factor that is permanently present during operational use, while the content of water vapor is variable as the relative humidity in the medium. The interaction of water vapor is dependent not only on the polymer absorption properties, but also on the product structure. This effect is particularly distinct in textile fabrics, where the fabric structure has a hierarchic character determined by complex systems of fibers with micrometric thickness, forming a yarn and the yarn threads form a higher structure such as thread repeat. The textile fabric structure intensifies absorption processes due to capillary processes that do not occur in monolithic products such as films or foils.



Figure 5. Effect of relative humidity (RH) of air in an isothermal medium on the volume resistivity " ρ_v " of PET woven fabric: (A) absolute humidity of woven fabric "W" = f(RH), (B) ρ_v = f(RH), (C) log ρ_v = f(W).

The importance of the problem of the air humidity effect in environment on the processes of current flow in a product in DC field was presented using an example of woven fabric made of 100% PET fibers. In order to do that, the isochronal current absorption and current depolarization in the woven fabric for 10 min were examined using an electrostatic field intensity of E = 1 kV/mm. The fabric was first purified and its surface weight was 100.0 g/m² and thickness of 0.2 mm. They used rigid electrodes with a diameter 50 mm and a constant unit load according to EN 1149-2:1999 + Ap1:2001, in a standard screened measurement system [16]. Before the tests, the woven fabrics were preheated to constant weight "m_s" considered as dry mass. Then, isothermal environment conditions were established (t = 23°C) under which the air relative humidity was changed from 25 to 88% followed by return to the initial humidity 25%. For each variant of RH in the range of 25–88%, the samples were air conditioning chamber Feutron. In parallel to the absorption and depolarization currents, the mass of moist fabric "m_w" was determined and then the absolute humidity of fabrics "W" was calculated from the dependence:

$$W = \left(\frac{m_w - m_s}{m_s}\right) \cdot 100\% \tag{6}$$

Figure 5 presents the effect of relative humidity (RH) of air in the isothermal medium on the volume resistivity " ρ_v " of PET woven fabric in the process of sorption followed by desorption.

Figure 5A shows that with increasing RH from 25 to 88%, the volume resistivity of PET woven fabric is decreased by about 1000 times. Changes in resistivity are nonlinear and conditioned by the modifying interaction of the molecules of water absorbed from air and physico-chemically and physically added to the fabric as shown by the sigmoidal character of the sorption and desorption isotherms (**Figure 5B**). Moreover, it is observed that the humidity and resistivity " ρ_v " depend on the way of reaching the physical equilibrium of sample by wetting or drying, which results in the hysteresis of humidity of fabrics and hysteresis of volume resistivity. The occurrence of hysteresis parameters proves how important is the definition of the fabric pre-conditioning and its acclimatization for tests.

The absolute humidity of woven fabric is an important factor influencing the processes of charge conductance and depolarization. For the PET woven fabric tested in the electrostatic field E = 1 kV/mm, the volume resistivity " ρ_{v} " of the fabric as a function of humidity "W" (**Figure 5C**) satisfy the generalized dependence:

$$\log \rho_v = -aW + b \tag{7}$$

where: *W*—absolute humidity of fiber, a = – 10.559, b = 16.150 (**Figure 5C**), which is consistent with the results of Morton and Hearle [20]. Based on the above dependence, one can estimate the volume resistivity of PET woven fabrics in the state of humidity W = 0% at a level of log $\rho_v = 16,150$ with correlation coefficient R² = 0.98.

3. Static electricity of polyesters

Polyesters form a group of polymers with a high susceptibility to static electricity and a long lifetime of charges generated on surface and in volume. This feature results from a low

number of free charges and a low electric conductance. On account of a high Debye radius, a charge can be formed in both the polymer top layer and volume [21]. The mechanism of static electricity of polymers is complex since the electric loading state attained constitutes a resultant effect of three partial processes: charge generation, charge storage on polymer surface, and in its volume and charge decay by relaxation and transport. Each of these partial processes proceeds differently in the case of so-called contact electricity, triboelectric, induction, injection in corona and glow discharges, γ -irradiated, laser–irradiated, and UV-irradiated electricity [22, 23]. It is the contact electricity that has been best known, particularly in polymer-metal systems, on account of the possible specification of molecular and energetic parameters for metals. Already in studies [24, 25], attempts have been undertaken to model contact electricity with the assumption that in the polymer counter-surface contact, the charge carriers are transferred from one surface to the other contacting surface, while the direction of charge transfer depends on parameters such as: work charge exit from contacting surfaces, surface temperature, and initial concentration of charge carriers.

The next question to be solved is the assessment of the carrier nature responsible for electricity. Many authors believe that electricity depends on the injection of electrons from/to the polymer surface [26, 27]. The mechanism of contact electricity with the polymer-metal system is considered when we use the notions of band structure of a solid body (insulator or semiconductor) to describe the polymer energetic structure. For polymers, the occurrence of a wide band of forbidden positions and a specified work of electron exit are assumed. A characteristic feature is the occurrence of discrete donor and acceptor energetic states in the band of forbidden energies. These states are localized at the edges of conduction and valence bands. The succession of the presence of discrete states is the broadening of band edges. According to Fuhrmann [28], Fabish [25], and Mizutani [29], these states can trap the charge carriers and take part in contact electricity.

Energetic states localized in the polymer top layer are energetically different as a result from the presence of impurities, free radicals, absorbed molecules, products of polymer oxidation, ends and branches of macromolecules, and structural defects. The nature of localized energetic states is also modified by the polymer physical microstructure, mainly by the content of crystalline phase, shape, and perfectness of crystallite and interphase structures: crystalliteamorphous zone. The use of the notion of trapping states is convenient for the description of the processes of charge displacement and accumulation in polymeric dielectrics. The filling of traps with various charges leads to a permanent presence of charges in polymer.

An open issue is the investigation method of the distribution of the charge generated in polymers. The knowledge of charge distribution is indispensable for the identification of electric conductance processes, strength of polymeric dielectrics, and their aging as well as the mechanisms of polarization in polymeric electrets. The classic methods of investigating the distribution of charges and electric relaxation of polymers include the methods thermally stimulated currents (TSC) and thermally stimulated depolarization currents (TSDC) [30]. The drawback of TSC and TSDC methods is their destructive character in relation to the sample tested. Apart from the thermally stimulated method, they developed acoustic methods suitable for a direct use in testing polymeric insulations under voltage, measurements of the distributions of electric fields [31, 32], and tracing the development of polarization in polymers under high field voltage. Three types of acoustic methods using different techniques of acoustic wave generation are now under improvement: laser induced pressure pulse (LIPP) [32], pressure wave propagation (PWP) [33], and electrically stimulated acoustic wave (ESAW) [34–36]. The analysis of signals from polymers affected by impulsing allows one to diagnose the space distribution of charge in polymers. According to the opinion of Motyl [37], the use of two measurement methods, for example, PWP and ESAW increases the reliability of results and extent the range of diagnosis. In PWP method, the deformation wave causes local changes in free and polarization charges in time, which is a source of the signal observed. In ESAW method, the applied voltage impulse to sample generates a signal from the whole charge and the homogeneously distributed dipoles are not detected.

3.1. Contact electricity in the PET film-metal system

Hennecke et al. [24] have proposed an analog model of polymer electricity consisting in contacting with metals in the interrupting way repeated until the charge is established. The qualitative interpretation is based on the concept of the band polymer model, where the occurrence of the energetic levels of forbidden bands and heights of barrier between these levels in polymer were taken into account. The static electricity of polymers with the repetition of contacts has been also analyzed by Fuhrmann [28], Fabish and Duke [25], Lowell [26] and Mizutani et al. [29]. Fabish and Duke have observed a reversible change in the sign of charge transferred on polymer from metals after successive contacts. These authors explain this phenomenon with the presence of charges in the form of molecular ions in the polymer top layer. These ions form local energetic states.

Mizutani et al. [29] have determined the properties of the metal-polymer contact by means of the photo-injection of electrons from metal (Cu, Al) to PET, indicating the existence of energetic states on the surface of PET. These researchers also assessed the density of surface states amounting to 1.7×10^{14} (cm⁻³ eV⁻¹) and confirmed a strong dependence of the contact energetic barrier on atmospheric conditions, including the presence of adsorbed oxygen molecules on the PET surface. Oxygen molecules, on account of a high affinity of electrons, can form surface states and act as electron traps. According to the opinion of Brennan et al. [38], during single and multiple contacts of polymer with counter-surface a charge is created whose range is limited to a depth of maximum 3 nm.

Lowell [26, 27] proposes a mechanism of charge transfer from metal to polymer (PET and PTFE). In the case of a single contact of polymer and metals (Al, Pt, and Hg), Lowell has found that the charge density does not depend on the type of metal. He puts forward a thesis that during a single contact, the tunneling of electrons occur from metal to traps in the polymer top layer, but the system does not reach thermodynamic equilibrium. The difference in electrostatic potentials created in the charge layer is inadequate to increase the energy of trap levels up to the Fermi energy of the metal. Only with a multiple contact, the charge is transferred to a higher depth. Then, it is possible to reach the equilibrium state. Lowell predicts the achievement of equilibrium charge density that will be linearly dependent on the metal work-function.

3.1.1. Contact electricity in the PET film-Al, PET film-Au systems

In this study, the susceptibility of PET film to static electricity in contact with metals (Al and Au) was investigated. Two pairs of cylindrical electrodes made of brass with a diameter of

50 mm and a height of 30 mm were used. Au and Al metals were evaporated onto the polished cylinder surface in the glow discharge aided with Argon. The coatings obtained were characterized by a high stability of the joint with the substrate, which made it possible to purify the surfaces before the tests of contact electricity. The PET films purified and devoid from charges were located between earthed electrodes in the following systems: Au-PET-Au and Al-PET-Al for 60s and then the electrodes were taken off in a frictionless way. The measurements of the sample surface charge were carried out in a contactless way by means of the probe of field intensity meter in the system described in paper [16]. During repeated contacts, the surface charge increased up to the saturation state that was obtained with the number of contacts of at least 100. The contact electricity was performed for PET film samples described in **Table 1**. The test results obtained are listed in **Table 2**.

3.1.2. Contact electricity of activated PET surface films

In this study, we also attempted to answer the question how the activation of PET surface influences its susceptibility to electricity. To that end, the films were subjected to an activating plasma treatment. The process was realized in a low-temperature plasma, in glow discharge RF under reduced pressure air with the use reactor system described in paper [39]. The test results were supplemented with the examinations of the sample volume and surface resistivity in DC field with the use of rigid Al electrodes.

In **Table 2** are listed the test results of volume and surface resistivity in contact with Al electrode, surface density of the charge were generated in contact with Au and Al metals. The resistivity was calculated on the basis of absorption and depolarization currents according to proceeding Badian [17]. The polarization component of the PET film surface free energy before and after the plasma treatment is also shown.

Based on the tests of the surface and volume resistance of untreated films (**Table 2**), one can think that the structural changes expressed by the crystallinity degree ranging from 7.4 to

ratio	At an an and the	-1 -	18PV	0 × 10 **	$\sigma \times 10^{-11}$	γ _p × 10 ⁻³ ,
Tacio	time, min.			C/cm ² , PET-Au	C/cm ² , PET-Al	N/m
R=2	0	15.776 ± 0.188	15.400 ± 0.157	-5.1 ± 3.0	-6.7 ± 3.0	10.5
	3	15.652 ± 0.148	15.075 ± 0.128	-3.3 ± 2.0	-4.2 ± 2.1	28.2
	10	15.615 ± 0.168	15.143 ± 0.209	-3.4 ± 2.0	-4.8 ± 1.5	32.2
	30	15.601 ± 0.211	15.114 ± 0.133	-0.7 ± 0.5	-2.7 ± 1.3	32.0
R=3,5	0	15.700 ± 0.043	15.500 ± 0.128	-6.6 ± 3.2	-8.8 ± 1.2	11.8
	3	15.553 ± 0.215	15.292 ± 0.165	-3.9 ± 1.3	-5.2 ± 1.3	30.4
	10	15.538 ± 0.204	15.281 ± 0.094	-2.4 ± 1.9	-4.0 ± 2.0	30.4
	30	15.580 ± 0.208	15.283 ± 0.232	-0.9 ± 0.5	-2.2 ± 1.0	32.8
R=4,0	0	16.306 ± 0.398	15.277 ± 0.177	-5.2 ± 4.0	-8.6 ± 3.5	11.1
	3	15.957 ± 0.080	15.095 ± 0.135	-3.0 ± 1.9	-3.6 ± 1.8	29.9
	10	15.932 ± 0.118	15.085 ± 0.143	-3.0 ± 2.0	-4.4 ± 2.7	33.5
	30	15.750 ± 0.190	14.952 ± 0.230	-0.9 ± 0.5	-2.0 ± 0.7	33.5

Table 2. Results of testing the surface properties of untreated and air plasma-treated PET films (power 100 W, flow 100sccm, pressure 20mTr).

19.8% and the Herman's coefficient of orientation from 0.12 to 0.58 do not influence, in a statistically significant way, the DC conduction in the top layer and volume of the films. Also, no significant effect of changes in physical structure on the level of charge generated in contact with Al and Au metals was found. On the other hand, a significant effect of the metal type on the charge value is observed. The density of charge generated on the PET film surfaces in contact with aluminum is higher than that in contact with gold. Let us assume Lewell hypothesis [26] that the value of static charge depends on the difference in the exit works of materials in contact. According to Davies [40], the values of the exit work of the material tested are arranged in the following sequence PET > Au > Al. This relation of exit works justifies the negative sign of charge generated on the PET surface in contact with metals, as well as the higher charge density in contact with aluminum compared to that in contact with gold.

The processes of static electricity of polymers are typical surface processes. The physicochemical and physical states of surface are of importance for the course of contact electricity processes. In this study, the physicochemical and physical properties of the PET film top layer were modified by air plasma treatment. The physicochemical properties of PET films were assessed by measuring the contact angle with water and methylene iodide and the free energy calculated according to procedure of Owens and Wendt [41]. In **Table 2** are listed the values of the polar component of the surface energy of films treated with plasma. The dispersion component was unchanged and therefore it was omitted. The plasma treatment was carried



Figure 6. Electron microscopy images of PET film surface, (A) untreated; treated with air plasma (power 100 W, flow 100 sccm, pressure 20 mTr): (B) 1 min, (C) 3 min, (D) 30 min. The arrows show the direction of films orientation.

out for 1–30 min. Already from 1 minute to 3 minutes, the plasma treatment strongly increases the polar component of the top layer of the PET films. The physicochemical changes result in a negligible decrease in the value of surface and volume resistivity of the films. The PET film surfaces modified with plasma in contact with Al and Au metals still show a negative charge, but the surface density of charge in PET films is significantly decreased. The generation of charges is the more weakened, the longer the surface was treated with plasma. These changes can be related to the surface physical state. The plasma interaction causes significant physical changes in the film surface microtopography. **Figure 6** shows the electron microscopic images of the PET film surfaces treated with plasma for 1, 3, and 30 min.

The effect of etching the polymer in its top layer that intensifies with increasing the plasma treatment time is observed. The surface is curved to form groove cavities located crosswise to the direction of stretching the film. The height of microroughness of surface subjected to plasma exposure for 30 min. With the strongest effect of etching can be assessed to about $0.04 \,\mu$ m. The character of surface carving is conditioned by the physical microstructure of PET. Based on the hypothesis of the polymer semi-crystalline structure, they are distinguished into two principal phases: crystalline and amorphous phases. The crystalline phase is characterized by a high energy of molecular cohesion that conditions its particular resistance to destructive factors, such as heat and the forces of interactions with plasma molecules. Considerably less resistant is the amorphous phase, in which the interaction between molecules are statistically incidental, and this phase is etched in the first place. In the image of the etched top layer, the protrusions seem to be formed by the crystalline phase of PET periodically occurring with long period in macro-fibrils. The etching effect generates the coarseness of surface that intensifies with prolonging the plasma action. The surface coarseness determines the real surface of film contact with metals. The coarser the surface, the lower is the charge that was found in measurements.

4. Polyester electrets

Electrets are materials in which a permanent electric charge occurs. The charge in electrets is stable for a longer time and its stability depends on the type of materials and exploitation conditions. It can last for years, while the material is an active source of electric field. The electrets are widely used in dust and gas filters, micro-machines, xerography, electro-acoustic transducers. Many electro-insulating polymers are used as electret precursors, including dipole (PET, PMMA and PS) and nondipole polymers (PTFE, PP and PE). The use of precursors in the form of films allows one to miniaturize the devices based on electrets. The charging state of electret material is obtained in various ways [22, 32, 46] using triboelectric effect (triboelectrets), DC electric field (thermo-electrets), UV and VIS radiations (photo-electrets), β and γ radiation (radio-electrets), glow and corona discharges (corona electrets).

Polyesters are materials with potential use as electret precursors owing to their susceptibility to dipole polarization and good mechanical parameters. Thermoelectrets are made by polymer polarization in DC electric field under conditions above the glass transition temperature and then after charging, they are refrigerated to freeze the state of oriented dipoles. The surface

charge formed is called heterocharge if its sign is opposite to the sign of electrode potential in contact and is connected with ordering the dipole polarization or the separation of already existing free charges. The homocharge has a sign consistent with the electrode potential sign in contact during the electret formation and shows the incorporation of charge carriers from electrode. During the formation of thermo-electret in the external electric field, the relaxation polarization component influences the process of dipole polarization.

Two types of the relaxation mechanisms were found: α - and β -relaxation. The former one occurs at temperatures above the glass transition temperature of PET or at a low field frequency, while β -relaxation appears at lower temperatures below the glass transition temperature of PET or at higher field frequencies. According to the present views, α -relaxation results from the co-operative motion of the kinetic units of macromolecule chain with discrete changes in the energy of orientation positions in the electric field. Groups $-O-CH_2-CH_2-O-$ and p-phenyl bonds are the kinetic units in PET. According to Saito et al. [13], the active kinetic units of polymer contain more than one mer macromolecule. Peruccini et al. [42] present the opinion that α -relaxation is an isotropic process and occurs in amorphous areas.

The process of β -relaxation occurs under conditions of a limited mobility of the main chain of macromolecule as a result of the rotation movements of single groups of atoms —(CO—O)— [6, 13, 43] with a stable dipole moment around the axis consistent with the axis of polymer orientation. Because of a considerable intermolecular interaction of the group of atoms, the process of β -relaxation shows an anisotropic nature [6, 13, 44, 45] and occurs in both amorphous and crystalline areas. Time changes leading to the stabilization of electret caused by relaxation processes and also by the effect of environmental conditions are known as aging [46, 47]. The study [16] describes the formation of thermo-electret from the PLA film precursor by isothermal polarization and demonstrates a stabilized density of surface charge and the dependence of charge level on the polarization intensity of filed E_{polar} and charging time. In the case of field intensity E_{polar} . < 20 MV/m, the heterocharge is observed that is stabilized in the processes of dipole relaxation and volume charge within 30 days. The use of higher field intensities E_{polar} . > 20 MV/m results in the transition of homocharge into heterocharge, which can be caused by the process of an additional injection of charge from electrodes or a change in the direction of dipole moment of molecular dipoles [48]. The prolongation of the PLA isothermal charging results in an increased charge density on the surface, which is consistent with the theory of isothermal dipole polarization, according to which the charge density exponentially depends on the charging time and relaxation time.

In the method of electret formation by irradiation with UV, VIS or ionizing β and γ , in the precursor electrons are excited from the basic state and the deep traps to the conduction band. The precursor in that time is in electric field, where a directed transport of charge carriers and trapping in new positions take place. Once the field and irradiation are turned off, the precursor shows a stable heterocharge. Zllangr et al. [23] analyzed the state of energetic traps the PET radio-electret made during the exposure to γ irradiation. The authors quantitatively characterized the average depth of trap level, density and distribution of traps by the technique of thermally stimulated currents (TSC). As precursor they used PET from various stages of production: an amorphous film, oriented in two directions and film crystallized in the process

of heating. The processes of molecular orientation, increasing the content of crystalline phase and irradiation caused an increase in the depth of localized states from 1.36 to 2.15 eV linearly with increasing the molecular orientation, from 1.20 to 1.40 eV with increasing the content of the PET crystalline phase and from 1.30 to 1.70 eV with increasing the dose of γ radiation. In the interpretation of authors [23], the processes of polymer crystallization, orientation of macromolecules and ionizing radiation cause new structural defects: on the crystallitesnoncrystalline border, along the border of oriented and nonoriented areas as well as cracked polymer macromolecules due to radiation, confirmed by a decrease in the molecular weight. An increase in defects generates new types of localized energetic levels, an increase in their number, decomposition, and depth. In the study [23] three models of traps are proposed, in relation to three methods of the PET treatment on the basis of quantitative data of TSC.

Currently, a great importance is ascribed to electrets in which a permanent charge is incorporated by the injection from external sources by means of corona or glow discharge [22, 49]. A charge is incorporated into polymer located in the zone of the electrode of crow discharge. Blade electrodes with a high potential generate in space electrons and various types of ions [50, 51] that recombine on the polymer surface, causing chemical changes and the residue diffuses into the polymer top layer and is trapped. During corona discharge, double bonds C = C and carbonyl groups are formed that can constitute additional traps for current carriers. Charges are accumulated near the polymer surface. The relative depth of charge localization related to the film thickness is assessed to 5%. Charging at increased temperature increases the stability of electret, which is exploited in the formation of pneumo-thermal nonwovens. The process effects are closely dependent on the gas composition and air humidity, if it proceeds under atmospheric conditions [52]. The mechanism of a permanent charge in material proceeds as in glow discharge. A decrease in the process pressure makes it possible to perform the synthesis of polymer and the simultaneous charging of the polymer that shows the features of electret [53].

5. Imparting electro-conductive and antistatic properties to polyesters

Polyesters (PET) have found their use as antistatic and electro-conductive materials. An increase in electric conductance of polyesters has been obtained to provide an effective dissipation of electrostatic charges and reduce electrostatic discharges. Owing to that, the use of polyester materials/fabrics has become safe, particularly in areas endangered with explosion and for workers using protective clothing. A high level of polyester conductance can be obtained by making polymeric composites. Composites are made according to two conceptions. The first one consists in combining at least two components, where the polymeric matrix is formed by polyester in which a conducting phase is scattered. The conducting phase can consist of: metal particle, carbon black, carbon fibers or nano-tubes, graphene, metal-lized fibers, conducting salts, and organic conductors, for example, conjugated polymers. The type of the scattered phase determines the electric conduction of composite. The scattered phase should be used in a quantity not lower than the percolation threshold. The value of

Type polyester substrate	Resistance related to the fabric square, $R_{\Box}\left[\Omega/cm^2\right]$					
	unmodified	Antistatized, non rubbed	Antistatized, rubbed (according to PN-EN ISO 105-X12)			
PLA	4.4±1.3 x1012	2.0±0.4 x104	6.1±0.5 x104			
PET	1.5±0.4 x1013	7.2±0.3 x10 ⁴	1.4±0.3 x105			
PC	3.6±0.8 x10 ¹¹	5.1±0.2 x104	7.5±0.7 x104			

Table 3. Test results of different kinds of antistatic polyester films coated with polypyrrole (test conditions t = 23° C, RH = 25°).

percolation threshold depends on the coefficient of the shape of conducting particles, their dimensions and arrangement in the matrix [54–56]. Particularly beneficial is the use of nanophase scattered in PET and PLA [57–64]. The lower the value of percolation threshold, the more beneficial are the mechanic properties of composite.

The other conception of making composites consists in coating the polyester surface (substrate) with the conducting phase. The examples of conducting phase include: metals condensed on polyester surfaces by the PVD technique [65], conjugated synthetic polymers such as polyaniline and polypyrrole [62–64] deposited by the "in situ" technique or CVD, carbon nano-tube, and graphenes deposited by the printing technique [61, 66–70].

Table 3 presents the results of our own studies obtained for conducting composites such as PET-PPy, PLA-PPy, PC-PPy with polypyrrole coating (PPy) deposited by the CVD method. Surface resistance measurements were carried out according to standard PN-EN ISO 3915. The specific resistance related to the fabric square, expressed as, R_{\Box} [Ω /cm²], was the quantitative parameter of resistance properties. The polypyrrole coating imparts antistatic properties to polyesters. The combination of PPy with PET substrates is stable and resistant to the mechanical wear conditions.

Antistatic polyester composites find many applications as conducting elements of electronic circuits, sensors, semi-transparent, and elastic electrodes in electronic-organic elements, optoelectronic and e-textiles, active layers, and transporting charge carriers in organic electroluminescent diodes and elements of organic solar cells.

6. Conclusions

The presentation of electric properties of polyesters including conventional and biodegradable polymers indicates that these polymers are continually an attractive group of materials. In polyesters, many problems concerning their behavior in electric DC field are still open as a subject of fundamental research. This type of thermoplastic polymers is continually subjected to various chemical and physical transformations, owing to which polyesters offer newer and newer solutions for the market and economy needs.

Acknowledgements

The manuscript was financed from funds assigned for 14-148-1-2118 statuary activity by Lodz University of Technology, Department of Material and Commodity Sciences and Textile Metrology, Poland.

Author details

Wieslawa Urbaniak-Domagala

Address all correspondence to: wurbando@p.lodz.pl

Department of Material and Commodity Sciences and Textile Metrology, Lodz University of Technology, Lodz, Poland

References

- [1] Burland DM, Miller RD, Walsh CA. Second-order nonlinearity in poled-polymer system. Chemical Reviews. 1994;94:31-75
- [2] Edge M, Hayes M, Mohammadian M, Allen NS, Jewitt T, Brems K, Jones K. Aspects of poly(ethylene terephthalate) degradation for archival life and environmental degradation. Polymer Degradation and Stability. 1991;2:131-153
- [3] Lengyel MA. Schottky emission and conduction in some organic insulating materials. Journal of Physics. 1966;**37**:807-810
- [4] Sacher E. Direct current conductivity of poly (ethylene terephthalate). Journal of Macromolecular Science, Part B: Physics. 1970;B4:441-448
- [5] Taylor DM, Lewis TJ. Electrical conduction in polyethylene terephthalate and polyethylene films. Journal of Physics D: Applied Physics. 1971;4:1346-1357
- [6] Gupta AK, Chand N, Mansingh A. Anisotropy of dielectric relaxation in poly(ethylene terephthalate) fibres. Polymer. 1979;20:875-878
- [7] Das-Gupta D. Conduction mechanisms and high-field effects in synthetic insulating polymers. IEEE Transactions on Dielectrics and Electrical Insulation. 1997;4:149-156
- [8] Das-Gupta D, Joyner K. On the nature of absorption currents in polyethyleneterephthalate (PET). Journal of Physics D: Applied Physics. 1976;9:829-840
- [9] Das-Gupta DK. Dielectric and related molecular processes in polymers. IEEE Transactions on Dielectrics and Electrical Insulation. 2001;8:6-14
- [10] Amborski LE. Structural dependence of the electrical conductivity of polyethylene terephthalate. Journal of Polymer Science Part A: Polymer Chemistry. 1962;62:331-346

- [11] Lilly AC, Mc Dowell JR. High-field conduction in films of mylar and teflon. Journal of Applied Physics. 1968;39:141-146
- [12] Kimball JC, Adams LW. Hopping conduction and super ionic conductors. Physical Review B. 1978;18:5851-5857
- [13] Saito S, Sasobe H, Nakajima T. Dielectric relaxation and electrical conduction of polymers as a function of pressure and temperature. Journal of Polymer Science Part A 2. 1968;6:1297-1315
- [14] Sawa G, Lee DC, Ieda M. Electric current with temperature variation arising from polymer-metal contacts. The Japanese Journal of Applied Physics. 1977;16:359-365
- [15] Wintle HJ. Charge motion and trapping in insulators surface and bulk effects. IEEE Transactions on Dielectrics and Electrical Insulation. 1999;6:1-10
- [16] Urbaniak-Domagala W. Electrical properties of polylactides. Journal of Electrostatics. 2013;71:456-461
- [17] Badian L. Effect of space charge on the properties of dielectrics. The Bulletin of the Polish Academy of Sciences. 1977;25:13-16
- [18] Strzałkowski A, Śliżyński A. Matematyczne metody opracowania wyników pomiarów. 2nd ed. PWN; 1978. p. 345
- [19] Razumova L, Rudakova T, Moisjew J, Mielnikow L, Zaikow G. Vysokomolekularne Sojedinienija A. 1975;17:pp. 861-864
- [20] Morton WE, Hearle JWS. Physical Properties of Textile Fibres. Manchester & London: The Textile Institute; 1962. pp. 457-484
- [21] Zahm M. Pole elektromagnetyczne. Warsaw, Poland: PWN; 1989
- [22] Hilczer B, Małecki J. Elektrety i piezopolimery. 2nd ed. Warsaw, Poland: PWN; 1992
- [23] Zllangr X, Zllou Y, Hang J. The mean depth of trap level of oriented, crystallized and ψ -irradited poly(ethylene terephthalate) electrets. In: Proceedings of the IEEE 7th International Conference on Electrets ISE 7; 25-27 October 1991; Berlin. pp. 55-59
- [24] Hennecke M, Hofmann R, Fuhrmann J. Simulation of contact electrification of polymers by an analogue model. Journal of Electrostatics. 1979;6:15-27
- [25] Fabish TJ, Duke CB. Molecular charge states and contact charge exchange in polymers. Journal of Applied Physics. 1977;48:4256-4266
- [26] Lowell J. The electrification of polymers by metals. Journal of Physics D: Applied Physics. 1976;9:1571-1585
- [27] Lowell J. Tunnelling between metals and insulators and its role in contact electrification. Journal of Physics D: Applied Physics. 1979;12:1541-1544
- [28] Fuhrmann J. Contact electrification of dielectric solids. Journal of Electrostatics. 1978;4: 109-118

- [29] Mizutani T, Takai Y, Osawa T, Jeda M. Barrier heights and surface states of metal-polymer (PET) contacts. Journal of Physics D: Applied Physics. 1976;9:2253-2259
- [30] Tomaszewicz W. Termicznie stymulowane prądy w nieuporządkowanych ciałach stałych. Poland: Politechnika Gdańska; 2005
- [31] Alquie C, Dreyfus G, Lewiner J. Stress-wave probing of electric field distributions in dielectrics. Physical Review Letters. 1981;47:1483-1487
- [32] Sessler GM, West JE, Gerhard G. High resolution laser pulse method for measuring charge distributions in dielectrics. Physical Review Letters. 1982;48:563-566
- [33] Tanaka A, Maeda M, Takada T. Observation of charge behavior in organic photoconductor using pressure-wave propagation method. IEEE Transactions on Electrical Insulation. 1992;27:440-444
- [34] Bernstein JB. Analysis of the electrically stimulated acoustic-wave method for observing space charge semi-insulating films. Physical Review B. 1991;44:10804-10814
- [35] Maeno T, Futami T, Kushibe H, Takada T, Cooke MC. Measurement of spatial charge distribution in thick dielectrics using the pulsed electroacoustic method. IEEE Transactions on Electrical Insulation. 1988;23:433-439
- [36] Motyl E. Pressure methods of space charge measurement in dielectrics. Journal of Electrostatics. 1997;40-41:469-476
- [37] Motyl E. Space charge in solid dielectrics. Analysis of measurement methods and investigations. Scientific Papers of the Institute of Electrical Engineering Fundamentals of the Wroclaw University of Technology. Monographs No.13. Poland. 2000
- [38] Brennan WJ, Lowell J, O'Neill M, Wilson MPW. Contact electrification: The charge penetration depth. Journal of Physics D: Applied Physics. 1992;25:1513-1517
- [39] Urbaniak-Domagała W, Krucińska I, Wrzosek H. Deposition of polypyrrole insulating layer on copper monofilaments using low temperature plasma technique. Materials Technology. 2009;**24**:24-28
- [40] Davies DK. Charge generation on dielectric surfaces. British Journal of Applied Physics: Journal of Physics. 1969;D2:1533-1537
- [41] Owens DK, Wendt RC. Estimation of the surface free energy of polymers. Journal of Applied Polymer Science. 1969;13:1741-1747
- [42] Pieruccini M, Ezquerra TA, Lanza M. Phenomenological model for the confined dynamics in semicrystalline polymers: The multiple α-relaxation in cold-crystallized poly(ethylene terephthalate). Journal of Chemical Physics. 2007;127:104903-104911
- [43] Saito S, Pratt GJ, Smith GJ, Michael JA. Dielectric relaxation spectroscopy of poly(ethylene terephthalate). Polymer International. 2002;51:21-26
- [44] Pop T, Iordache D, Jonas A. Dielectric properties of PET below its glass transition temperature. Microelectronic Engineering. 1997;33:377-384

- [45] Dargent E, Bureau E, Delbreilh L, Zumailan A, Saiter JM. Effect of macromolecular orientation on the structural relaxation mechanisms of poly(ethylene terephthalate). Polymer. 2005;46:3090-3095
- [46] Sessler GM, editor. Electrets. Topics in Applied Physics. New York: Springer-Verlag; 1980
- [47] McGonigle EA, Daly JH, Jenkins SD, Liggat JJ, Pethrick RA. Influence of physical aging on the molecular motion and structural relaxation in poly(ethylene terephthalate) and related polyesters. Macromolecules. 2000;33:480-489
- [48] Piekara AH. Polarization reversal in electrets and hydrogen bonding. Journal of Electrostatics. 1975;1:209-216
- [49] Viraneva A, Yovcheva T, Mekishev G. Pressure effect on the polymer electret films. IEEE Transactions on Dielectrics and Electrical Insulation. 2013;20:1882-1886
- [50] Herous L, Nemamcha M, Remadnia M, Dascalescu L. Factors that influence the surface potential decay on a thin film of polyethylene terephthalate (PET). Journal of Electrostatics. 2009;67:198-202
- [51] Ignatova M, Yovcheva T, Viraneva A, Mekishev G, Manolova N, Rashkov I. Macromo lecular nanotechnology: Study of charge storage in the nanofibrous poly(ethylene terephthalate) electrets prepared by electrospinning or by corona discharge method. Euro pean Polymer Journal. 2008;44:1962-1967
- [52] Rouagdia K, Nemamcha M, Herous L, Dascalescu L, Mellouki H. Surface potential decay of DC-corona-charged PET films on humid electrodes. Journal of Electrostatics. 2015;78:17-21
- [53] Wertheimer MR, Klemberg-Sapieha JE, Schreiber HP. Advances in basic and applied aspects of microwave plasma polymerization. Thin Solid Films. 1984;115:109-124
- [54] Bin Y, Kitanaka M, Zhu D, Matsuo M. Development of highly oriented polyethylene filled with aligned carbon nanotubes by gelation/crystallization from solutions. Macromolecules. 2003;36:6213-6219
- [55] Nuzhnyy D, Savinov M, Bovtun V, Kempa M, Petzelt J, Mayoral B, McNally T. Broadband conductivity and dielectric spectroscopy of composites of multiwalled carbon nanotubes and poly(ethylene terephthalate) around their low percolation threshold. Nanotechnology. 2013;24:1-9
- [56] Hegde RR, Bhat GS, Deshpande B. Crystallization kinetics and morphology of meltspun poly(ethyleneterephthalate) nanocomposite fibers. Express Polymer Letters. 2013;7:821-831
- [57] Pietrzak Ł, Jeszka JK. Nanokompozyty polilaktyd/wielościenne nanorurki węglowe -Otrzymywanie i właściwości elektryczne. Polimery. 2010;7-8:524-528

- [58] Żenkiewicz M, Richert J, Rytlewski R, Richert A. Wybrane *właściwości elektryczne* i cieplne kompozytów *polilaktyd*/grafit. Polimery. 2011;**6**:489-493
- [59] Czarnecka P, Ciach T, Kunicki A, Olszyna A, Gołaszewska M, Jastrzębska A. Otrzymy wanie i właściwości włókien nanokompozytowych *polilaktyd*-tlenek glinu. Inżynieria Materiałowa. 2010;**31**:467-469
- [60] Gorrasi G, Bugatti V, Milone C, Mastronardo E, Piperopoulos E, Iemmo L, Di Bartolomeo A. Effect of temperature and morphology on the electrical properties of PET/conductive nanofillers composites. Composites Part B: Engineering. 2018;135:149-154
- [61] Li Z, Luo G, Wei F, Huang Y. Microstructure of carbon nanotubes/PET conductive composites fibers and their properties. Composites Science and Technology. 2006;66:1022-1029
- [62] Tessier D, Dao L, Zhang Z, King MW, Guidoin R. Polymerization and surface analysis of electrically-conductive polypyrrole on surface-activated polyester fabrics for biomedical applications. Journal of Biomaterials Science. Polymer Edition. 2000;11:87-99
- [63] Zhang L, Meng S, Zhang Z. Electroactivity and stability of polylactide/polypyrrole composites. Journal of Biomaterials Science. 2011;22:1931-1946
- [64] Wu CS. Preparation and characterization of an aromatic polyester/polyaniline composite and its improved counterpart. Express Polymer Letters. 2012;6:465-475
- [65] Januszkiewicz Ł, Hausman S, Krucińska I, Nowak I. Textile vee antena made with PVD process. International Journal of Applied Electromagnetics and Mechanics. 2014;46:361-365
- [66] Skrzetuska E, Puchalski M, Krucińska I. Chemically driven printed textile sensors based on graphene and carbon nanotubes. Sensors. 2014;14:16816-16828
- [67] Urbaniak-Domagała W, Skrzetuska E, Komorowska M, Krucińska I. Development trends in electronics printed: Intelligent textiles produced with the use of printing techniques on textile substrates. In: Yun I, editor. Printed Electronics—Current Trends and Applications. Chapter 7. Rijeka, Croatia: InTech; September 28, 2016. DOI: 10.5772/61800
- [68] Skrzetuska E, Urbaniak-Domagała W, Lipp-Symonowicz B, Krucińska I. Giving functional properties to fabrics containing polyester fibres from poly (ethylene terephthalate) with the printing method. In: Saleh HE-DM, editor. Polyester. Rijeka, Croatia: InTech; September 9, 2012. ISBN 978-953-51-0770-5
- [69] Krucińska I, Skrzetuska E, Urbaniak-Domagała W. Prototypes of carbon nanotubebased textile sensors manufactured by the screen printing method. Fibres & Textiles in Eastern Europe. 2012;20:79-83
- [70] Kordas K, Mustonen T, Toth G, Jantunen H, Lajunen M, Soldano C, Talapatra S, Kar S, Vajtari R, Ajayan PM. Inkjet printing of electrically conductive patterns of carbon nanotubes. Small. 2011;8-9:1021-1025

Breakdown Characteristics of Varistor Ceramics

Jianying Li, Kangning Wu and Yuwei Huang

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.79720

Abstract

Breakdown characteristics are of great importance for varistor ceramics, which largely depend on Schottky barriers at grain boundaries. In order to enhance breakdown performance for meeting the requirement of device miniaturization, different doping methods are introduced to not only restrict grain size from additional phase but also manipulate defect structure of Schottky barrier at grain boundaries from substitution. Distribution of barriers is another key point affecting breakdown characteristics in varistor ceramics. Dimensional effect, which is detected in not only ZnO ceramics but also CaCu₃Ti₄O₁₂ ceramics, is practically and theoretically found to be closely correlated with uniformity of grains. As a result, breakdown characteristics of varistors are dominated by combination effect of single barrier performance and spatial barrier distribution. In this chapter, enhanced breakdown field in Ca_xSr_{1-x}Cu₃Ti₄O₁₂ ceramics, in situ synthesized CaCu₃Ti₄O₁₂-CuAl₂O₄ ceramics, and CaCu₃Ti₄O₁₂-Y_{2/3}Cu₃Ti₄O₁₂ composite ceramics are investigated from the aspect of Schottky barriers at grain boundaries. In addition, dimensional effect is found in both ZnO and CaCu₃Ti₄O₁₂ ceramics, which are investigated from grain size distribution through theoretical and experimental analysis.

Keywords: breakdown characteristics, varistor ceramics, Schottky barrier, $CaCu_3Ti_4O_{12}$ ceramics, ZnO ceramics

1. Introduction

Varistor ceramics exhibit excellent nonlinear current-voltage (*I-V*) characteristics that they are widely employed for overvoltage protection in power system and electronic circuits. Zinc oxide (ZnO) varistor ceramics is one typical varistor ceramics, which has been for decades widely employed in arrestors [1]. The breakdown field of commercial ZnO varistor ceramics is commonly 200–300 V/mm and the nonlinear coefficient is ~50. Besides, perovskite CaCu₃Ti₄O₁₂ (CCTO) ceramics exhibit giant permittivity and nonlinear characteristics that

IntechOpen

© 2018 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

made them potential candidates for application in surge absorption [2, 3]. Varistor ceramics consist of grains and grain boundaries, and it is grain boundary which manipulates the breakdown field. Breakdown field is commonly suggested to be dominated by single grain boundary and the amount of grain boundaries along electric field direction. The single grain boundary electrical performance is determined by Schottky barriers which are primarily comprised of positively charged depletion layers and negatively charged interface states [4]. Meanwhile, the amount of grain boundaries is decided by grain size. With the progress of device miniaturization, the demand for varistor ceramics with high breakdown field and highenergy absorption capability needs to be fulfilled. In order to enhance breakdown characteristics, microstructure of varistor ceramics should be improved which can be summarized into decreasing grain sizes on one hand and enhancing single barrier performance on the other hand. Two major ways of achieving greater breakdown characteristics are (1) improving preparation method and (2) finding a better recipe which might contain additives [5–10]. For improved preparation process, lots of methods like nano-sized particles and spark plasma sintering (SPS) techniques are induced to reduce the grain sizes [11, 12]. Doping is another typical topic in enhancing breakdown performance in varistor ceramics. As is known in ZnO varistor ceramics, nonlinear properties do not exist until Bi₂O₃ is added which forms an intergranular layer and manipulates defect structure to form better Schottky barriers at grain boundaries. Later on, Sb₂O₃, Co₂O₃, Mn₂O₃, etc. are added to further enhance breakdown field and improve nonlinear performance. As for CCTO varistor ceramics, several doping methods were introduced which have different effects on microstructure. Firstly, the doping ions are able to substitute ions in CCTO lattice (Ca²⁺, Cu²⁺) and form a relatively homogeneous structure [5]. This method dominantly manipulates Schottky barrier structure at grain boundaries. Secondly, another phase is formed besides CCTO phase resulting in heterogeneous structure, like SrTiO₃, TiO₂, CuAl₂O₄, etc. [6–8]. The additional phases mainly restrict the growth of grains and control the grain size to produce more grain boundaries. Thirdly, to form another CCTO-like phase with CCTO phase, like $Y_{2/3}Cu_3Ti_4O_{12}$ [9], is also suggested. This method not only introduces heterogeneous structure which restricts grain growth but also induces more defects at grain boundaries to enhance Schottky barriers. In summary, these three methods of doping result in diverse improvement of electrical characteristics due to various effects on microstructure of varistor ceramics. In the main text, these three kinds of doping methods are, respectively, introduced in detail.

Besides methods of enhancing breakdown characteristics, a non-negligible phenomenon that electrical performance is not uniform in the bulk of the ceramics should be taken into consideration for design and practical application. The inhomogeneous electrical properties at the cross section have been widely reported. About 5–11% of cross-section region in varistor ceramics was found to exhibit lower breakdown voltage than the rest of the regions [13]. This further results in current localization, which causes electrical puncture, thermal cracking, or even thermal runaway [14]. In addition, dimensional effect, which exhibits as the thickness dependence of breakdown field, is found in not only ZnO ceramics but also CCTO ceramics [15–17]. It is found that breakdown field and nonlinear coefficient are significantly decreased below a critical thickness, which brings much trouble in designing. The spatial electrical nonuniformity was widely attributed to inhomogeneous grain size distribution and grain
boundary characteristics. Electrical measurements using microcontact on single grain boundary suggested that 50% grain boundaries can be defined as "good," 30% are "bad," and the rest are ineffective [18]. At the same time, reports from luminescence created by electrical breakdown also provide support for uneven grain boundaries [19]. In this work, the structural origin of dimensional effect in varistor ceramics is investigated through experiment and simulation, which suggested that wide grain size distribution should be responsible. After careful processing of controlling grain sizes into narrower distribution, dimensional effect is diminished, which, to some extent, proves the responsibility of grain size distribution.

2. Enhancement of electrical breakdown field in varistor ceramics

2.1. Enhanced breakdown field in Ca_{1-x}Sr_xCu₃Ti₄O₁₂ ceramics via tailoring donor density

2.1.1. Phase composition and surface morphology

X-ray diffraction (XRD) patterns of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ceramics are presented in **Figure 1**. Main perovskite phase of CCTO is detected with small amount of impurity phase of CuO and SrTiO₃ in **Figure 1(a)**. In the enlarged view of (220) peak in **Figure 1(b)**, the peak gradually moves to a lower angle with the increase of Sr/Ca ratio, indicating increased lattice constant as a result of Ca²⁺ (0.99 Å) with smaller radius being substituted by Sr²⁺ (1.26 Å).

SEM images and corresponding grain size distribution are shown in **Figure 2**. Grain size of the samples is smaller than that in CCTO ceramics (>8 μ m), while it changes little on the ratio of Sr/Ca (2.4–2.8 μ m). Energy dispersive X-ray spectroscopy (EDS) is further measured at the marked regions in **Figure 2** with the results listed in **Table 1**. No pure CaCu₃Ti₄O₁₂ or SrCu₃Ti₄O₁₂ is detected, indicating solid solution systems. Major discrepancy for those large



Figure 1. XRD patterns of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ variator ceramics.



Figure 2. Backscattering SEM pictures of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ceramic samples. (a) Sr0.2-Ca0.8, (b) Sr0.4-Ca0.6, (c) Sr0.6-Ca0.4 and (d) Sr0.8-Ca0.2. (usage permitted by Elsevier).

Atom (%)	Sr0.2-Ca	Sr0.2-Ca0.8		Sr0.4-Ca0.6		Sr0.6-C	Sr0.6-Ca0.4		Sr0.8-Ca	Sr0.8-Ca0.2	
	A1	A2	B1	B2	B3	C1	C2	C3	D1	D2	
ОК	66.68	70.31	62.31	68.99	72.75	59.20	65.93	63.45	67.67	73.60	
Ti K	17.14	15.49	0.86	16.20	14.22	6.70	17.11	18.65	16.66	13.73	
Cu K	11.94	10.64	36.82	10.74	9.44	32.87	12.70	13.80	11.51	9.50	
Sr L	0.85	0.28		1.69	1.14	0.88	3.33	3.15	3.26	2.40	
Ca K	3.39	3.27		0.71	0.46		3.54	3.31	3.66	3.08	

Table 1. EDS results for marked points in Figure 2 (usage permitted by Elsevier).



Figure 3. Current-voltage (*J*-*E*) characteristics (a) and impedance spectra (b) of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ceramics at room temperature.

grains (A1, B2, C2, D1) and small grains (A2, B3, C3, D2) is found to be Sr/Ca ratio. The higher Sr/Ca ratio in larger grains indicates Sr²⁺ might have benefit for grain growth in relatively low temperatures.

2.1.2. Enhanced breakdown field and complex impedance spectra

Figure 3 is current density-electric field (*J*-*E*) curves of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ ceramics. The breakdown field E_{1mA} and nonlinear coefficient α are calculated:

$$E_{1\mathrm{mA}} = U_{1\mathrm{mA}}/d,\tag{1}$$

$$\alpha = \frac{1}{\log(U_{1\text{mA}}/U_{0.1\text{mA}})},$$
(2)

where U_{1mA} and $U_{0.1mA}$ are the voltage under current density of 1 and 0.1 mA/cm², respectively, and *d* is the sample thickness. The corresponding α and E_{1mA} are listed in **Table 2**. Enhanced E_{1mA} are observed in Ca_{1-x}Sr_xCu₃Ti₄O₁₂ especially for samples with Sr/Ca ratio of 0.4/0.6. It increased remarkably to 24.52 kV/cm, which is as twice as that of CCTO. Elevated E_{1mA} can be partially ascribed to decreased grain size. However, greatly varied E_{1mA} are found in samples with similar grain size of ~2.5 µm in **Figure 2**, indicating grain size is not decisive. Series connected *RC* units are widely employed for characterizing properties of grains and grain boundaries based on the fact that CCTO ceramics consist semiconducting grains and insulating grain boundaries [2, 20]. The complex impedance *Z** can be expressed as:

$$Z^* = Z' - iZ'' = \frac{R_{\rm gb}}{1 + i\omega R_{\rm gb} C_{\rm gb}} + \frac{R_{\rm g}}{1 + i\omega R_{\rm g} C_{\rm g}},$$
(3)

where R_{gb} and C_{gb} are resistance and capacitance of grain boundaries while R_g and C_g are resistance and capacitance of grains. R_g and R_{gb} can be thus obtained as intercepts in complex impedance spectra in **Figure 4**. In addition, resistance activation energies of grain (E_g) and grain boundary (E_{gb}) are calculated via the Arrhenius equation. As shown in **Table 2**, R_g and E_g remain constant to ~225 Ω and ~0.13 eV, while R_{gb} and E_{gb} vary significantly. Highest R_{gb} and E_{gb} of 9900 M Ω and 1.03 eV are obtained for samples with Sr/Ca ratio of 0.4/4.6, which is in accordance with breakdown field in **Figure 3(a)**. Consequently, it is reasonable to deduce that modified grain boundary characteristics that are crucial for the improved breakdown field.

Generally, the barrier height ϕ_0 depends on the depletion layer width x_d , interface state density N_s , and donor concentration N_d :							
α	6.83	8.11	8.24	8.32			
E _{1mA} (kV/cm)	15.88	24.52	7.28	6.15			
$R_{ m g}\left(\Omega ight)$	221	221	234	233			
$R_{ m gb} \left({ m M} \Omega ight)$	640	9900	270	12			
$E_{\rm g}~({\rm eV})$	0.14	0.13	0.14	0.13			
$E_{\rm gb}~({\rm eV})$	1.01	1.03	0.86	0.71			

Back-to-back Schottky barrier at grain boundary is crucial for the nonlinearity of varistors.

2.1.3. Tailoring of donor density

Table 2. Parameters for electrical nonlinearity and inhomogeneity of grain and grain boundary of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ varistor ceramics.

$$\phi_0 = \frac{eN_s^2}{8\varepsilon_0\varepsilon_r N_d}.\tag{4}$$

For single grain boundary, the grain boundary capacitance of unit area C_0 under zero biased voltage is $C_0 = [e\varepsilon_r N_d/(8\phi_0)]^{1/2}$, while the capacitance *C* under a bias voltage *U* is as follows [21]:

$$\left(\frac{1}{C} - \frac{1}{2C_0}\right)^2 = \frac{2(\phi_0 + U)}{e\varepsilon_r N_d}.$$
(5)

Dependence of $(C^{-1} - 1/2C_0^{-1})$ on *U* is plotted in **Figure 4**, showing good nonlinearity. Barrier parameter is calculated and listed in **Table 3**. N_d for all the samples is almost constant, while N_s varies remarkably from 3.3×10^{13} cm⁻³ for Sr0.4-Ca0.6 to 15.6×10^{13} cm⁻³ for Sr0.8-Ca0.2. Consequently, the highest barrier height is obtained in Sr0.4-Ca0.6 and lowest in Sr0.8-Ca0.2, which matches the results of E_{gb} from impedance spectra.

Oxygen vacancy is considered as origin of electron formation due to weak cation—O bonds. Space of *A* site in CCTO is rather rigid as the observed Ca—O distance is 2.61 Å, while the



Figure 4. C-V characteristics of Ca_{1-x}Sr_xCu₃Ti₄O₁₂ varistor ceramics.

Samples	Sr0.2-Ca0.8	Sr0.4-Ca0.6	Sr0.6-Ca0.4	Sr0.8-Ca0.2
φ ₀ (eV)	1.11	1.17	0.96	0.40
$x_{\rm d}$ (nm)	630	880	460	240
$N_{\rm s}~(10^9~{\rm cm}^{-2})$	7.73	5.90	9.20	7.53
$N_{\rm d}~(10^{13}~{\rm cm}^{-3})$	6.11	3.34	9.99	15.67

Table 3. Parameters of Schottky barrier of $Ca_{1-x}Sr_xCu_3Ti_4O_{12}$ varistor ceramics (usage permitted by Elsevier).

expected value is 2.72 Å [22]. Radius of Sr is much larger than that of Ca so that Sr—O bonds are extremely over bonded. In increasing the ratio of Sr/Ca, larger Sr stretches the Ti—O bonds, leading to enhanced polarizability of the tilted TiO₆ octahedra and possible breaking of the balance of Cu—O plane. Therefore, oxygen vacancy is much easier to be produced as well as segregated Cu-rich secondary phase, shown in **Figure 1** [23].

On the contrary, oxygen vacancy may be inhibited due to solid solution effect between SCTO and CCTO. Taking Sr^{2+} in CCTO as an example, besides Sr_{Ca} , Sr exists as Sr_{Cu} and Sr_i^- as Cu^{2+} is easily loss in CCTO. Sr-Cu distortion is likely formed due to the same valence of Sr, Ca, and Cu ions. Increased *A* site ions can coordinate with the O^{2-} in TiO₆ octahedron. Moreover, Sr_i^- can compensate the electrons generated by oxygen vacancies. As a result, declined donor density is thus formed, which can result from Ca in SCTO as well. Maximum integrated action of strong solid solution effect and weak Sr stretching effect is achieved when Sr/Ca ratio is 40/ 60, which leads to greatly elevated potential barrier height more than 1.0 eV and enhanced breakdown field consequently.

2.2. In situ synthesized CCTO-xCuAl₂O₄ varistor ceramics

2.2.1. Preparation and characterization of in situ synthesized CCTO-xCuAl₂O₄ samples

CCTO powders are prepared via traditional solid-state reaction method and suspended in $Al(NO_3)_3$ aqueous solution. Subsequently, the suspension was quantitatively titrated with NH_4OH to make $Al(OH)_3$ precipitate on the surface of CCTO particles. After drying, the powders are calcined at 950°C for 4 h to dehydrate $Al(OH)_3$ into Al_2O_3 . Finally, they were pressed into pellets and sintered in air at 1100°C for 4 h.

XRD patterns are presented in **Figure 5(a)**. Only single phase of CCTO can be detected when x = 0. With increased precipitation of Al³⁺, another spinel phase CuAl₂O₄ is found. Backscattering



Figure 5. XRD patterns (a) and SEM picture (b) of in situ synthesized CCTO-*x*CuAl₂O₄ ceramics (usage permitted by IOP Publishing).

SEM picture of CCTO-0.4CuAl₂O₄ sample is further taken as shown in **Figure 5(b)**, in which three typical regions, A, B, and C, can be observed. According to EDS results presented in **Table 4**, element distribution of the gray grains (A, 15–20 μ m in size) is similar to CCTO with a little Al. The black grains (B1, B2, and B3, 1–4 μ m in size) are found to be the secondary phase, while the bright region of C is Cu-rich intergranular phase. It is proposed that Cu₂O and CuO are easily precipitated over 1000°C as Cu-rich phase, which is the main source for CuAl₂O₄. The involved chemical reactions can be expressed as:

$$2Al(OH)_{3} = Al_{2}O_{3} + 3H_{2}O\uparrow$$

$$CuO + Al_{2}O_{3} = CuAl_{2}O_{4}$$

$$Cu_{2}O + 2Al_{2}O_{3} + \frac{1}{2}O_{2} = 2CuAl_{2}O_{4}.$$
(6)

Surface morphology of the samples is characterized by SEM as shown in **Figure 6**. For CCTO ceramics, little secondary phase is found, and the average grain size is 19.1 μ m as shown in **Figure 6(a)**. As to samples with *x* = 0.4 found in **Figure 6(b)**, numbers of small particles appear in interior and intergranular region of CCTO grains, and the average grain size is 18.8 μ m. When *x* increases to 0.5 and 0.65, average grain sizes decrease notably to about 1.6 μ m. It is proposed that reduction of grain size may arise from the depleted Cu-rich phases, which assists grain growth in forming CuAl₂O₄ according to Eq. (4). Pinning effect of CuAl₂O₄ phase could further inhibit the grain growth, which generally obeys the Zener model:

Atom (%)	Α	B1	B2	B3	С
ОК	41.97	39.6	44.64	50.37	37.81
Al K	1.42	41.55	28.38	19.70	0.79
Ca K	6.56	0.61	2.26	3.12	1.10
Ti K	28.81	2.60	9.35	12.44	5.17
Cu K	21.25	15.63	15.37	14.37	55.13

Table 4. EDS results of in situ synthesized CCTO-0.4CuAl₂O₄ sample in Figure 5(b) (usage permitted by IOP Publishing).



Figure 6. SEM images of CCTO-xCuAl₂O₄ ceramic samples: (a) x = 0, (b) x = 0.4, (c) x = 0.5, and (d) x = 0.65 (usage permitted by Elsevier).

Breakdown Characteristics of Varistor Ceramics 67 http://dx.doi.org/10.5772/intechopen.79720

$$\frac{G}{r} = \frac{4}{3}f^{-1},$$
 (7)

where *G* is the limit size of the matrix grain and *r* and *f* are particle diameter and volume fraction of the secondary phase, respectively. The grain size of the secondary phase decreases, and the volume fraction of the secondary phase increases; the matrix grain size apparently declines. Therefore, the best pining effect is achieved in the sample with x = 0.5 for relatively small grain size and high volume fraction of the spinel phase.

2.2.2. Enhanced breakdown field in CCTO-xCuAl₂O₄ ceramic samples

J-E characteristics of in situ synthesized CCTO-xCuAl₂O₄ ceramics are plotted in **Figure 7**, and the corresponding E_{1mA} and α are plotted in the inset. It is clear that E_{1mA} of samples with x = 0.5 increased sharply to about 21 kV/cm with reduced grain size. On this basis, it is proposed that aggregation of CuAl₂O₄ and the inhibiting of grain growth should take responsibility for the greatly enhanced E_{1mA} . Although $E_{1mA} = 4.3$ kV/cm is found in x = 0.65 samples with similar grain size of ~1.6 µm, it can be ascribed to abnormally large grains as presented in **Figure 6(d)**.

For comparison, CuAl_2O_4 is directly introduced into CCTO by solid-state reaction method following the same sintering condition. Dependence of α and $E_{1\text{mA}}$ on addition of the secondary phase is plotted in **Figure 7(b)**. Similar to the in situ synthesized samples, the highest $E_{1\text{mA}}$ is achieved when x = 0.5. However, its highest $E_{1\text{mA}}$ is only about 15 kV/cm. This suggests that enhanced $E_{1\text{mA}}$ in directly induced samples mainly arise from pinning effect while additional depletion of Cu-rich phase should be also considered for in situ synthesized samples.

2.2.3. Complex impedance analysis for CCTO-xCuAl₂O₄ samples

Figure 8(a) is complex impedance spectra of CCTO-*x*CuAl₂O₄ samples at 393 K. R_{gb} increases greatly from 0.37 to 13.55 MΩ with increased Al. Based on the dominant effect of R_{gb} to the overall resistance, DC conductivity can approximate to conductivity of grain boundary. Activation energy of DC conductivity can be thus calculated via the Arrhenius equation, as shown



Figure 7. J-E characteristics of in situ synthesized (a) and directly induced (b) CCTO-xCuAl₂O₄ samples.



Figure 8. Impedance spectra (a) and temperature dependence of DC conductivity (b) of CCTO-xCuAl₂O₄.



Figure 9. XRD patterns (a) and SEM picture (b) of 0.2CCTO-0.8YCTO ceramics (usage permitted by Elsevier).

in **Figure 8(b)**. Highest energy of 0.81 eV is found for samples with x = 0.5, indicating inhibited hopping conduction process in them. Thus, it is suggested that the new formation of insulating phase CuAl₂O₄ may modify the electronic structure of grain boundaries and improve the electrical properties of CCTO ceramics. The enhanced R_{gb} can be attributed to higher activation energy required for hopping conduction at grain boundary.

2.3. CCTO-YCTO composite ceramics with enhanced nonlinearity

2.3.1. Phase composition and surface morphology

 $(1 - x)CaCu_3T_4O_{12}-xY_{2/3}Cu_3T_4O_{12}$ [(1 - x)CCTO-xYCTO] ceramics were prepared via solidstate reaction method. They were sintered in air at 1100°C for 10 h. XRD patterns are shown in **Figure 9(a)**, in which the main phase of perovskite phase and small amount of CuO, TiO₂, and $Y_2Ti_2O_7$ are detected. With increased Y^{3+} , (200) peak moves to lower angle. However, it is hard to identify CCTO with YCTO phase due to similar lattice structure. Therefore, EDS is conducted (**Figure 9(b)** and **Table 5**). Element distribution of the large gains (4–6 µm) is close to YCTO, while small grains (1–2 µm) are close to CCTO although solid solution is found.

Atom (%)	A1	A2	A3	B1	B2
ҮК	4.00	4.6	4.56	0.89	0.85
Ca K	0.87	0.61	0.94	4.90	4.76
Cu K	9.08	8.29	7.98	9.15	10.34
Ti K	20.49	19.41	19.89	20.77	21.77
ОК	64.86	66.09	65.62	64.29	61.89

Table 5. EDS results of 0.2CCTO-0.8YCTO sample in Figure 9(b) (usage permitted by Elsevier).



Figure 10. Surface morphology of (1 - x)CCTO-*x*YCTO ceramics: (a) x = 0, (b) x = 0.5, (c) x = 0.8, and (d) x = 1.0.

SEM pictures were taken, as shown in **Figure 9**. Large grains are formed in pure CCTO and YCTO ceramics with Cu-rich phase segregated in the intergranular region marked by red circles as shown in **Figure 10(a)** and **(d)**. Discontinuous distribution of grain size is finally formed in CCTO samples. Stripy grains in pure YCTO ceramics suggest that sintering temperature is so high that grains could not hold the hexagonal shape. Meanwhile, two kinds of grains, with grain sizes of 4–6 μ m and 1–2 μ m, respectively, were found uniformly distributed in composite ceramics. Average grain size is reduced, which indicates that grain growth of CCTO and YCTO was suppressed by each other in the form of pinning effect.

2.3.2. Enhanced electrical nonlinearity

J-E characteristics at room temperature are presented in **Figure 11**. E_{1mA} of 0.5CCTO-0.5YCTO and 0.2CCTO-0.8YCTO are enhanced to 10.17 and 11.24 kV/cm, respectively, which are approximately 10 times of that 1.24 kV/cm of CCTO sample. α is improved to 9.57 and 9.88, respectively, as well. Although extremely high α is reported in some reports, they are hard to be repeated. α largely depends on the current range used for calculation in Eq. (2) and the measuring method. As shown in **Figure 11(b)**, some reports of high α are actually ~5 in the current range 0.1–1 mA/cm in ln*J*–ln*E* plots [24–26]. The reported high α might also originate from positive feedback of heat generated from thermal emission process at grain boundary.

Complex impendence spectroscopy at room temperature is plotted in **Figure 12**. R_g is close to 20–40 Ω , and R_{gb} varies significantly up to 1200 M Ω in samples with x = 0.8, while it is 55.5 M Ω in pure CCTO. To further explore the carriers' migration across barrier, E_g and E_{gb} are calculated in **Table 6**. Similar to other reports, E_g is constant while E_{gb} differs significantly, inferring crucial role of grain boundary on carrier transport. E_{gb} gradually increases with increased x, suggesting gradually developed Schottky barrier with the addition of YCTO. The barrier



Figure 11. *J*-*E* characteristics of (1 - x)CCTO-*x*YCTO ceramics (a) and some reported CCTO ceramics with high nonlinear coefficient (b).



Figure 12. Complex impedance spectra of (1 - x)CCTO-xYCTO ceramics.

Energies	ССТО	0.5CCTO-0.5YCTO	0.8CCTO-0.2YCTO	усто
E _g (eV)	0.10	0.09	0.09	0.08
$E_{\rm gb}~({\rm eV})$	0.69	1.11	1.50	031

Table 6. Activation energies of grain and grain boundary resistance of (1 - x)CCTO-xYCTO samples.

height of sample with x = 0.8 reaches a maximum of 1.50 eV, which is twice higher than 0.69 eV of CCTO. The high barrier height leads to high nonlinear coefficient, which is consistent with results of *J*-*E* performance shown in **Figure 11(a)**.

Grain boundary resistance dominates the conduction process. So the hopping conduction is deduced, inhibiting improved grain boundary resistance and activation energy in composite ceramics. This inhibition may arise from increased number of grain boundaries or enhanced blocking effect of single barrier. There are three types of grain boundaries: CCTO/YCTO, CCTO/CCTO, and YCTO/YCTO. E_{gb} of 0.2CCTO-0.8YCTO samples (1.43 eV) is higher than that 1.11 eV of 0.5CCTO-0.5YCTO samples, indicating effect of grain boundary type is more important. Assuming both CCTO and YCTO grains are cubic, its surface area ratio can be simply written as:

$$\frac{A_{\rm CCTO}}{A_{\rm YCTO}} = \frac{r_{\rm CCTO}^2 \times (\rm Vol\%_{\rm CCTO}/\rm Vol_{\rm CCTO})}{r_{\rm YCTO}^2 \times (\rm Vol\%_{\rm YCTO}/\rm Vol_{\rm YCTO})} = \frac{r_{\rm YCTO} \times \rm Vol\%_{\rm CCTO}}{r_{\rm CCTO} \times \rm Vol\%_{\rm YCTO}},$$
(8)

where *A* is surface area of grains, *r* is grain size, Vol is single grain volume, and Vol% is volume fraction. Densities of CCTO and YCTO are 5.05 and 5.20 g/cm³, respectively. The average grain sizes for CCTO and YCTO are 1.24 and 4.57 μ m according to results found in **Figure 10(b** and **c**). On this basis, it can be obtained that A_{CCTO}/A_{YCTO} for 0.5CCTO-0.5YCTO is 0.38, while it is 0.95 for 0.2CCTO-0.8YCTO. In other words, the number of CCTO/YCTO interfaces reaches maximum in 0.2CCTO-0.8YCTO sample. On one hand, solid solution between Y³⁺ and Ca²⁺ could inhibit generation of donors, leading to thicker depletion layers. On the other hand, more interface states are produced at the YCTO/CCTO heterojunction. As a result, barrier height is improved so that more energy is needed for carriers to migrate across barriers.

3. Dimensional effect of varistor ceramics

3.1. Phenomenon of dimensional effect

Thickness dependence of $E_{1\text{mA}}$ and α of ZnO ceramics with low, medium, and high potential gradients is plotted in **Figure 13(a)**. Similar phenomenon is also found in CCTO ceramics in **Figure 13(b)**. Every curve exhibits a turning point corresponding to sample thickness *d*. Critical thickness d_{cr} critical breakdown field E_{cr} and critical nonlinear coefficient α_{c} are determined by each curve. Such behavior can be empirically represented as:

$$E_{1\mathrm{mA}} \propto e^{bd}$$
, (9)

where the exponent *b* represents the transitional behavior for the entire curve. Let this exponent in $d < d_c$ domain be denoted as b_1 while it is denoted as b_2 in the $d > d_c$ domain, i.e.:

$$\ln E_{1mA} = a_1 + b_1 d \ (d < d_c), \tag{10}$$

$$\ln E_{1mA} = a_2 + b_2 d \ (d > d_c). \tag{11}$$

The summary of the parameters b_1 , b_2 , d_c , and E_c in **Figure 13** is listed in **Table 7**. d_c significantly decreases with increased E_{1mA} and E_c , which indicate that those who exhibit higher E_{1mA} exhibit less severe dimensional effect. At the same time, b_2 slightly decreases with



Figure 13. Thickness dependence of E_{1mA} and α of (a) ZnO ceramics and (b) CCTO ceramics.

Samples		b_1	<i>b</i> ₂	<i>d</i> _c (mm)	E _c (V/mm)
ZnO ceramics	High	9.4	0.21	0.19	185
	Medium	18.6	0.31	0.28	110
	Low	6.0	0.36	0.98	33
CaCu ₃ Ti ₄ O ₁₂ ceramics		0.278	0.087	0.90	53

Table 7. The exponents b_1 and b_2 , critical thickness d_{cr} and the transitional breakdown field E_c of ZnO ceramics and CCTO ceramics in **Figure 12**.

increased E_{1mA} , suggesting more stable E_{1mA} with variation of thickness. However, no matter what variators are used in high-voltage or low-voltage situations, dimensional effect undoubtedly exists, which brings much trouble for practical application and design. Therefore, further investigation of dimensional effect is needed for stable electrical performance.

3.2. Simulation of dimensional effect

Breakdown voltage of single grain boundary is acknowledged to be nearly constant (\sim 3 V), indicating other factors should be responsible for dimensional effect. To understand the structural origin of dimensional effect, a model based on the network of grains and grain boundaries is proposed. Grain sizes in varistor ceramics fit the normal distribution, in which the probability density *f*(*l*) can be expressed as:

$$f(l) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left[-\frac{\left(l-\mu\right)^2}{2\sigma^2}\right],\tag{12}$$

where *l* is the average grain size, σ is the standard deviation, and μ is the mathematical expectation. For ceramics with diameter of *D* and thickness of *d*, it is assumed that all grains are cubic with length of *m*; the number of grains on the cross-section *N* is thus calculated as:

Breakdown Characteristics of Varistor Ceramics 73 http://dx.doi.org/10.5772/intechopen.79720

$$N = \frac{\pi D^2}{4\mu^2}.$$
(13)

It is assumed that these *N* grains on the cross section lead to *N* grain chains along thickness direction. Since *l* also fits normal distribution, the average grain number should be d/m, and the variance of the average grain size should be $\sigma^2/(d/m)$; therefore:

$$f(\bar{l}) = \frac{1}{\sqrt{2\pi} \frac{\sigma}{\sqrt{d/\mu}}} \exp\left[-\frac{(\bar{l}-\mu)^2}{2\frac{\sigma^2}{d/\mu}}\right].$$
 (14)

The amount of chains with grain sizes from \overline{l} to $\overline{l} + \Delta \overline{l}$ fits:

$$\Delta n(l) = N f(l) \Delta l, \tag{15}$$

Another assumption is that the current that went through one grain chain is independent on other chains. On this basis, the relationship between the voltage and the current in one grain chain can be expressed as:

$$V = \frac{d}{\bar{l}} V_B + I_i(\bar{l}) \frac{d}{\Delta n(\bar{l}) \mu^2} \rho_{g'}$$
(16)

where $V_{\rm B}$ is the breakdown voltage of single grain boundary and $\rho_{\rm g}$ is the electrical resistivity of grain. Consequently, the total current in this piece of ceramics should be the sum of current flowing in *N* grain chains:

$$I = \sum I_i(\bar{l}). \tag{17}$$

Based on the model above, *J*-*E* characteristic under a fixed thickness can be acquired with increased applied voltage *V*, and the E_{1mA} is able to be calculated. With variance of *d* in Eq. (12), a series of *J*-*E* curves are acquired, and E_{1mA} corresponding to different thicknesses are therefore known. According to grain size distribution of the measured ZnO varistor samples with high and medium E_{1mA} found in **Figure 13(a)**, average grain size *m* and variance σ^2 are calculated and taken into the model. Hence, the thickness dependences of E_{1mA} are plotted in **Figure 14**. The d_c of high-voltage varistors is ~0.2 mm, whereas it is ~0.3 mm for medium-voltage varistors. Both d_c and E_c from simulation fit the experimental results in **Figure 13(a)** well, proving the effectiveness of the proposed model.

In addition, if the average grain size is fixed, sample thickness *d* is reversely proportional to the variance of the average grain size. The maximum of the probability density $f(\mu)$ fits:

$$f(\mu) = \frac{1}{\sqrt{2\pi} \frac{\sigma}{\sqrt{d/\mu}}}.$$
(18)

With increased d, f(m) increases, indicating a narrower grain size distribution. Therefore, dimensional effect of varistor ceramics originated from the thickness dependence of grain size variance.



Figure 14. The thickness dependence of breakdown field via simulation (usage permitted by Elsevier).

As for CCTO ceramics which also exhibits dimensional effect shown in Figure 13(b), SEM images and grain size distribution on longitudinal section morphologies are investigated, as shown in **Figure 15**. Grains are smaller near the surface, whereas they are larger and denser in the interior. Quantitative analysis shows that grain sizes are more uniform near the surface while the size distribution is wider in the interior. The average grain size increased from 20.23 µm near the surface to 23.94 µm in the interior, while the porosity decreased from 4.95% near the surface to 0.33% in the interior. Although the grains with size below 30 μ m are dominant in number, they contribute less to the section area. It can be seen in Figure 15(b), (d), and (f) that although grains with size below 15 μ m contribute to more than 50% of grains, the sum of their occupied area is less than 10%. Despite small increase of average grain size from the surface to interior part, the major grain size that contributed to section areas is significantly different. On the surface, amount of the grains between 20 and 40 µm is most, while grains between 40 and 60 µm dominate the section area. Especially, the grain size range extends to 50–90 μ m in the interior. From this point, it can be deduced that nonuniform distribution of grain size indeed contributed to dimensional effect in varistor ceramics, which is in accordance with simulation discussed above.

3.3. Elimination of dimensional effect

In not only ZnO varistor ceramics but also CCTO ceramics, dimensional effect exists because of nonuniform grain size distribution, which restricts its practical application. Therefore, in order to diminish or to attenuate dimensional effect, it is important to make grain size distribution more uniform. Despite the traditional processed ZnO varistor ceramics (Tr), another amine processed (Am) samples are prepared. At first, ZnO is dissolved in NH₄(OH) and NH₄(HCO₃)



Figure 15. SEM of cross-section morphologies, grain area, and grain size distribution at the surface (a and b), near the surface (c and d), and in the interior (e and f) of CCTO ceramics (usage permitted by Elsevier).

solution with other additives in solutions, which is consequently heated to 110°C. After careful monitoring and controlling the pH of this mixed solution to 8–9, the precipitations are separated from the solution by filtration and washed with diethylamine solution to remove all chloride ions. When the solution is dried, the remained powders are calcined at 500°C, and then traditional processes are followed.



Figure 16. SEM pictures for (a) traditional processed and (b) amine processed ZnO varistors (usage permitted by Elsevier).

SEM photos of traditional processed (Tr) and amine processed (Am) ZnO samples are shown in **Figure 16(a)** and **(b)**, respectively. Lots of small grains are scattered between compactly aligned big grains in Tr samples, as shown in **Figure 16(a)**. However, no such small grains are seen in Am samples. The grains in Am samples are more uniform than those in Tr samples. Lots of grains with size below 3 μ m exist in Tr samples, while the grains are compact with almost no grains with size below 3 μ m.

Thickness dependence of $E_{1\text{mA}}$ of Tr and Am samples are depicted in **Figure 17**. Tr samples exhibit distinct dimensional effect with d_c of 0.28 mm. Notably, the Am samples show lower



Figure 17. Thickness dependence of E_{1mA} for traditional processed (Tr) ZnO varistors and amine processed (Am) ZnO varistors with identical recipe and processing variables (usage permitted by Elsevier).

 $E_{1\text{mA}}$ but exhibit no distinct dimensional effect. The decreased $E_{1\text{mA}}$ might be attributed to larger average grain size in Am samples than that in Tr samples. What is evident is that uniform grain sizes are obtained, which could effectively eliminate dimensional effect.

4. Conclusion

Breakdown characteristics in varistor ceramics are investigated from grain boundary characteristics based on single barrier performance and barrier distribution. On one hand, different methods of doping including substitution and additional phase result in not only restriction on grain sizes but also manipulation of defects in Schottky barriers of varistor ceramics to enhance breakdown field to meet the requirement of device miniaturization. In addition, restriction on further decreased thickness of varistor ceramics is found as dimensional effect in not only ZnO ceramics but also $CaCu_3Ti_4O_{12}$ ceramics. From theoretical analysis and experimental results, the dimensional effect is found closely related with the uniformity of grain sizes, which influence the distribution of grain boundaries quite well. Consequently, the breakdown characteristics in varistor ceramics are understood from the aspect of single barrier performance and spatial distribution of barriers.

Author details

Jianying Li*, Kangning Wu and Yuwei Huang

*Address all correspondence to: lijy@xjtu.edu.cn

State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an, China

References

- Matsuoka M. Nonohmic properties of zinc oxide ceramics. Japanese Journal of Applied Physics. 1971;10:736-746. DOI: 10.1143/JJAP.10.736
- [2] Sinclair DC, Adams TB, Morrison FD, West AR. CaCu₃Ti₄O₁₂: One-step internal barrier layer capacitor. Applied Physics Letters. 2002;80:2153-2155. DOI: 10.1063/1.1463211
- [3] Chung SY, Kim ID, Kang SJ. Strong nonlinear current-voltage behaviour in perovskitederivative calcium copper titanate. Nature Materials. 2004;3:774-778. DOI: 10.1038/nmat1238
- [4] Blatter G, Greuter F. Carrier transport through grain boundaries in semiconductors. Physical Review B. 1986;33:3952-3966. DOI: 10.1103/PhysRevB.33.3952

- [5] Tang Z, Huang Y, Wu K, Li J. Significantly enhanced breakdown field in Ca_{1-x}Sr_xCu₃Ti₄O₁₂ ceramics by tailoring donor densities. Journal of the European Ceramic Society. 2018;**38**:1569-1575. DOI: 10.1016/j.jeurceramsoc.2017.11.018
- [6] Li J, Jia R, Tang X, Zhao X, Li S. Enhanced electric breakdown field of CaCu₃Ti₄O₁₂ ceramics: Tuning of grain boundary by a secondary phase. Journal of Physics D: Applied Physics. 2013;46:325304. DOI: 10.1088/0022-3727/46/32/325304
- [7] Jia R, Zhao X, Li J, Tang X. Colossal breakdown electric field and dielectric response of Aldoped CaCu₃Ti₄O₁₂ ceramics. Materials Science and Engineering: B. 2014;185:79-85. DOI: 10.1016/j.mseb.2014.02.015
- [8] Li J, Hou L, Jia R, Gao L, Wu K, Li S. Influences of CuAl₂O₄ doping on the dielectric properties of CaCu₃Ti₄O₁₂ ceramics. Journal of Materials Science: Materials in Electronics. 2015;26:5085-5091. DOI: 10.1007/s10854-015-3033-0
- [9] Li J, Wu K, Jia R, Hou L, Gao L, Li S. Towards enhanced varistor property and lower dielectric loss of CaCu₃Ti₄O₁₂ based ceramics. Materials & Design. 2016;92:546-551. DOI: 10.1016/j.matdes.2015.12.073
- [10] Tang Z, Wu K, Huang Y, Li J. High breakdown field CaCu₃Ti₄O₁₂ ceramics: Roles of the secondary phase and of Sr doping. Energies. 2017;10:1031. DOI: 10.3390/en10071031
- [11] Chaim R, Chevallier G, Weibel A, Estournes C. Grain growth during spark plasma and flash sintering of ceramic nanoparticles: A review. Journal of Materials Science. 2018;53: 3087-3105. DOI: 10.1007/s10853-017-1761-7
- [12] Pourrahimi AM, Liu D, Strom V, Hedenqvist MS, Olsson RT, Gedde UW. Heat treatment of ZnO nanoparticles: New methods to achieve high-purity nanoparticles for high-voltage applications. Journal of Materials Chemistry A. 2015;3:17190-17200
- [13] Eda K. Destruction mechanism of zno varistors due to high currents. Journal of Applied Physics. 1984;56:2948-2955. DOI: 10.1063/1.333836
- [14] Smeets R, van der Linden WA. Verification of the short-circuit current making capability of high-voltage switching devices. IEEE Transactions on Power Delivery. 2001;16:611-618. DOI: 10.1109/61.956746
- [15] Li J, Li B, Zhai D, Li S, Alim MA. Dielectric response on the critical breakdown field in ZnO varistors. Journal of Physics D-Applied Physics. 2006;39:4969-4974. DOI: 10.1088/ 0022-3727/39/23/011
- [16] Li J, Jia R, Hou L, Gao L, Wu K, Li S. The dimensional effect of dielectric performance in CaCu₃Ti₄O₁₂ ceramics: Role of grain boundary. Journal of Alloys and Compounds. 2015; 644:824-829. DOI: 10.1016/j.jallcom.2015.05.095
- [17] Li ST, Li JY, Alim MA. Structural origin of dimensional effect in ZnO varistors. Journal of Electroceramics. 2003;11:119-124. DOI: 10.1023/B:JECR.0000015668.26785.89

- [18] Hohenberger G, Tomandl G, Ebert R, Taube T. Inhomogeneous conductivity in varistor ceramics: Methods of investigation. Journal of the American Ceramic Society. 2010;74: 2067-2072. DOI: 10.1111/j.1151-2916.1991.tb08260.x
- [19] Greuter F, Blatter G. Electrical-properties of grain-boundaries in polycrystalline compound semiconductors. Semiconductor Science and Technology. 1990;5:111-137. DOI: 10.1088/0268-1242/5/2/001
- [20] Adams TB, Sinclair DC, West AR. Giant barrier layer capacitance effects in CaCu₃Ti4O₁₂ ceramics. Advanced Materials. 2002;14:1321. DOI: 10.1002/chin.200251017
- [21] Mukae K, Tsuda K, Nagasawa I. Capacitance-vs-voltage characteristics of ZnO varistors. Journal of Applied Physics. 1979;50:4475. DOI: 10.1063/1.326411
- [22] Li J, Subramanian MA, Rosenfeld HD, Jones CY, Toby BH, Sleight AW. Clues to the giant dielectric constant of CaCu₃Ti₄O₁₂ in the defect structure of "SrCu₃Ti₄O₁₂". Chemistry of Materials. 2004;16:5223-5225. DOI: 10.1021/cm048345u
- [23] Schmidt R, Pandey S, Fiorenzad P, Sinclairb DC. Non-stoichiometry in "CaCu₃Ti₄O₁₂" (CCTO) ceramics. RSC Advances. 2013;3:14580-14589. DOI: 10.1039/C3RA41319E
- [24] Ramírez MA, Bueno PR, Varela JA, Longo E. Non-Ohmic and dielectric properties of a Ca₂Cu₂Ti₄O₁₂ polycrystalline system. Applied Physics Letters. 2006;89:212102. DOI: 10.1063/ 1.2393122
- [25] Ribeiro WC, Araujo RGC, Bueno PR. The dielectric suppress and the control of semiconductor non-Ohmic feature of CaCu₃Ti₄O₁₂ by means of tin doping. Applied Physics Letters. 2011;98:323. DOI: 10.1063/1.3574016
- [26] Thongbai P, Boonlakhorn J, Putasaeng B, Yamwong T, Maensiri S. Extremely enhanced nonlinear current-voltage properties of Tb-doped CaCu₃Ti₄O₁₂ ceramics. Journal of the American Ceramic Society. 2013;96:379-381. DOI: 10.1111/jace.12157

Measurement Methods and Extraction Techniques

Measurement Methods and Extraction Techniques to Obtain the Dielectric Properties of Materials

Turgut Ozturk and Muhammet Tahir Güneşer

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.80276

Abstract

Material characterization plays an important role in many applications that are called as security, military, communication, bioengineering, medical treatment, food industry, and material processing, since it is useful to identify other properties such as stress-strain relation, bio content, moisture content, materials density, etc. Therefore, the dielectric properties of materials should be achieved with high accuracy using appropriate measurement techniques and extraction techniques. There are many measurement methods to obtain the dielectric properties of materials, which can be divided into two categories: up conversion and down conversion methods. A microwave measurement method can be called as frequency up conversion, while THz time-domain spectroscopy (THz-TDS) system is a frequency down conversion method. The selection of more convenient measurement method depends on some parameters such as frequency range, material phase, and temperature. In this chapter, the measurement methods and extraction techniques will be discussed, and alternative ways will be presented with experimental and simulation results.

Keywords: complex permittivity, dielectric materials, free space measurement, material characterization, Newton-Raphson, terahertz radiation, THz, time-domain spectroscopy

1. Introduction

The complex permittivity of materials is independent of available measurement methods. This parameter has an important place for material characterization in electrical and electronics engineering. It can be used to recognize the interaction between a material and an electromagnetic radiation. In many applications, knowing of some parameters of the material, which is

IntechOpen

© 2018 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

cheaper than trial-error method, facilitates the work of engineers. Therefore, materials characterization and measurement methods are increasingly gaining importance at mm waves and THz frequency ranges. For instance, the knowledge of behavior of materials in these frequency ranges is essential to design and produce new equipment for astronomy or remote sensing applications.

It is possible to divide the measurement methods into two categories as up and down frequency conversion methods. In this context, the optical measurement methods can be called as a down-conversion method, and its aim is to decrease the frequency from 10^{14} Hz to 10^{12} or 10^{11} Hz. The well-known down conversion (optical) measurement method is Terahertz timedomain spectroscopy (THz-TDS). Usually, a femtosecond laser source is used to excite receiver and transmitter photoconductive antennas. Millimeter wave or microwave measurement methods can be called as an up-conversion method because of using frequency extenders to obtain the hundreds of GHz, and the purpose of it is to increase the frequency from 10^{10} Hz to 10^{11} Hz. The most preferred method is free space measurement (FSM) method in this category. Generally, a sample is placed between two horn antennas, and the measurement process is controlled by a Vector Network Analyzer (VNA).

Many different extraction techniques were investigated to obtain the high accuracy for the dielectric parameters, and they are usually divided into two groups as analytical (Nicolson-Ross-Weir [NRW] or NIST Iterative) and numerical (Newton-Raphson or Genetic Algorithm) techniques. In addition, the artificial intelligence (AI) methods are used to extract the dielectric properties to provide support the numerical techniques. To obtain the dielectric constant, numerical techniques are preferred to eliminate the associated error between sample thickness and frequency. However, there is an initial value problem in this approach. Therefore, both analytical and numerical techniques should be tried to achieve the most accurate result.

2. Dielectric properties of materials for material characterization

The dielectric properties of a material are related to other properties of that material. Humidity and temperature in the environment, the density of the material, its structure, the amount of water in it, and the porosity can change the dielectric properties of the material for the frequencies of microwave, millimeter wave, and THz [1, 2]. Besides, the thickness of the material, the chemical composition, and especially, the permanent dipole moment also affect the dielectric properties of a material. In addition, the effects of electromagnetic interference are needed to take in the account considering the environmental conditions [3].

The complex permittivity, which is an internal characteristic of material independent of the measurement technique, is accepted an important value of material characterization for electrical engineering [4]. Dielectric constant and loss tangent, which are electrical characteristics of material, play an important role in the propagation of the electromagnetic energy in the insulating medium. Therefore, the permittivity determines the propagation speed of the electromagnetic wave and the amount of stored energy on the material.

The dielectric properties of a material consist of relative dielectric constant (ε_r) and magnetic permeability constant (μ_r), which are represented by the equations $\varepsilon = \varepsilon_0 \varepsilon_r$ and $\mu = \mu_0 \mu_r$. $\varepsilon_0 = 8.52 x 10^{-12} (F/m)$ and $\mu_0 = 4\pi x 10^{-7} (H/m)$ are the values of permittivity and permeability of the cavity, respectively [5]. When an electromagnetic wave is applied to a material, the interaction of the material is expressed by two basic functions: permittivity and permeability. The complex permittivity consists of real and imaginary parts as seen on Eq. 1 [6]:

$$\varepsilon = \varepsilon_r - j\varepsilon_i \tag{1}$$

where ε_r is real, which represents stored electric field energy on the material, and ε_i is imaginary, which is amount of electric field loss. In case j = -1 on Eq. 1, the rate of imaginary $(\varepsilon_i / \varepsilon'')$ over real $(\varepsilon_r / \varepsilon')$ is called as loss tangent seen on Eq. 2.

$$\tan\left(\delta\right) = \varepsilon_i / \varepsilon_r \tag{2}$$

The imaginary part is also correlated with electrical conductivity (σ) as seen on $\varepsilon_i = \sigma/\varepsilon_0 \omega$, where ω is angular frequency. Orthogonal axis representation of real and imaginary parts of complex permittivity is seen in **Figure 1**.

The propagation of the electromagnetic wave in a material depends on its permittivity and permeability. When the impedance of the waveguide in the material (Z) is lower than free space impedance (Z_0), impedance mismatch occurs. During the propagation through the material, some of the energy are transmitted, and some are also reflected. In other words, material and electromagnetic wave interaction occur in three ways: reflection, absorption, and transmission [5].

Propagation speed of the waveguide through the material (v_m) is lower than speed of light (c). Since the frequency (f) is constant, the wavelength (λ_m) is seen shorter than free space



Figure 1. Representation of complex permittivity.



Figure 2. Interaction of electromagnetic wave with material.

wavelength (λ_0). Transition and propagation of a waveguide to a single layer material are seen in **Figure 2** [7].

In an electromagnetic field, propagation paisley expression of a transverse electromagnetic (TEM) plane wave on +z direction is displayed as $E(z, \omega) = E_0 e^{-\gamma_z}$, where the angular frequency is calculated as $\omega = 2\pi f$ and γ represents the propagation of the waveguide [8].

3. Measurement methods

Two different measurements, which are optic and microwave methods, are used in material characterization processes of THz frequency range. THz waves have unique properties such as being able to pass through some materials, which are not so permeable for other parts of the electromagnetic spectrum, or reflecting from some materials close to 100%, being harmless compared to X-rays, and having the ability to distinguish between different materials. The change of wavelength and frequency related to the THz gap is shown in **Figure 3**.

The time-domain spectroscopy (TDS) system, which is created in parallel with technological developments, is still expensive due to its most important component femtosecond lasers, and



Figure 3. Showing a part of electromagnetic spectrum.

it is generally not reliable and stable enough for long-term industrial use. To solve the problems of laser source in TDS system, Multimode Laser Diode (MLD), which is smaller, simpler, cheaper, stable, and commercially available, is used alternatively. Although MLD-TDS is weaker than traditional THz-TDS in terms of radiant power, radiation efficiency, and spectrum width, it has been shown in some studies that these points can be improved [9–11].

The microwave measurement systems including frequency up conversion methods are actively used in material characterization processes in THz frequency domain as an alternative to conventional TDS systems. However, only one of these methods cannot be used effectively on whole frequency band to measure the dielectric properties of the material. Moreover, several difficulties were seen in measuring lossy and low-loss materials with high accuracy. Therefore, different methods are needed for each band and material loss [6, 12]. The factors, such as measured frequency range, the expected value of the permittivity, required measurement accuracy, properties of the material (homogeneous, isotropic), and form of the material (solid, liquid, and gas), must be taken into consideration during the method determination. In addition, conditions such as sample size constraints, temperature, contact/noncontact measurement, and destructive/nondestructive measurement must be considered [12, 13].

Although the analyzed material differs according to where they are applied, the basic process is to completely determine the dielectric properties. In this framework, researches have been carried out on the analysis of many kinds of materials, and the results are shared. Some researches attempted to determine the effects of ambient conditions, which are created for the preservation of foods and preservation of freshness for a long time in food industry, on the material by the change in the permittivity [14, 15]. Successful studies have been conducted to examine the effect of changes in humidity on the freshness of the food [16, 17].

There is no single measurement technique for all conditions in the direction of these items. For this reason, a more precise measurement can be performed after determining which measurement method is suitable. If desired frequency range is high, free space measurement (FSM) method is the most suitable one by considering current technology.

3.1. Free space measurement method

Since the fact that it is aimed to work in THz frequency range, free space measurement method that is one of microwave measurement methods is at the foreground due to many advantages. FSM method especially offers the possibility of especially nondestructive and noncontact measurements, characterization of solid-liquid-powder materials, and measuring solid materials except very small ones.

Generally, measurement techniques, which are used in microwave and millimeter wave frequency regions, can be classified into two groups as resonant and nonresonant methods. Materials can be analyzed at single or discrete frequencies with resonant method. But with the nonresonant method, the analysis of materials can be pursued over a wide frequency band [6]. Recently, the most preferred methods of analysis for frequency bands above 1 GHz are listed as waveguide, coaxial probe, resonant cavity, and free-ambient measurement method [5, 18].

Nonresonant methods are used to determine electrical and magnetic properties over a wide frequency range, but resonant methods are better suited for calculating only single frequency [19]. Commonly used methods, which are including basic functions that must be included in a measurement method, are compared in **Table 1**, where ND is Nondestructive, S is Solid, L is Liquid, and G is Gas [5, 6]. Some of these techniques are more suitable for solid materials and others for liquids. It is also important that the analysis method is simple, as well as cheap [20].

FSM method has better dynamic capacity and spectral resolution than other methods [21]. However, FSM method could not be widening unless development of measuring devices for last decade [22]. Thus, measurement of the complex permittivity is possible over a wide frequency range by means of advanced measuring equipment and the FSM method accurately [23]. The FSM method consists of two antennas connected to a Vector Network Analyzer (VNA), and between the two antennas a sample holder in which the material to be measured is placed as shown in **Figure 4** [9, 24].

The quartz plates are not required in measurement setup if measurements are taken for solids like Teflon or glass. Because sagging of solid materials can be neglected when the sample

	FSM	Waveguide	Coaxial probe
Dielectric features	ε _r -μ _r	ε _r -μ _r	ε _r
S-parameter	<i>S</i> ₁₁ - <i>S</i> ₂₁	<i>S</i> ₁₁ - <i>S</i> ₂₁	<i>S</i> ₁₁
Frequency band	Wide	Discrete	Wide
Dimension	Large	Medium	Little
Testing procedure	ND	Destructive	ND
Sample preparation	Easy	Hard	Easy
Form of material	S-L-G	S	S-L
Monitoring	Very easy	Hard	Easy

Table 1. Comparison of commonly used microwave measurement methods.



Figure 4. Schematic representation of FSM method.

holder is properly placed [7]. VNA is standard equipment of microwave and millimeter wave measurement systems for simultaneous measurement of S-parameters, which are used for calculating dielectric features of materials [22].

3.1.1. Features of FSM method

The accuracy of the measurements is increased by a high time domain solution with FSM method, even requiring a simple test setup for installation [25]. FSM method provides to measure S parameters under the conditions as contactless, nondestructive, and high temperature with wide frequency range and different substance forms and especially for nonhomogeneous materials. It is preferred to coaxial and waveguide measurement methods, since it does not need sample preparation [18, 26]. Another disadvantage of waveguide method is seen as leakage around the sample and limitation of sizing sample [27]. Moreover, waveguide and coaxial measurement methods both need for proper preparation of the sample. This requirement causes limitation of measurement accuracy for nonprocessable substances [28].

Spot focus can be achieved using lenses that will minimize the diffraction effect for high accuracy measurements [23, 26]. The antenna gain can also be increased, thanks to lenses that align the beam and reduce the diameter [29]. Additionally, the measurement errors can be reduced by TRL calibrations and VNA gating techniques [27]. Selecting the size of the sample larger also provides reduction of the diffraction effect. But larger specimens cause sagging problem especially nonrigids [7]. Even when the optimum thickness is achieved at the sample, another measurement error can be seen because the phase that is on the sample may not be planar. To prevent this, the effect of thickness must be taken into account in order to match the center of the sample with the point of the thinnest beam, which is aligned through the lens [30].

3.1.2. Measurement with FSM method

A software was developed for analysis and defining the material. Therefore, firstly, the materials, which had been analyzed in microwave and millimeter wave frequency bands, were measured and compared with other studies in the literature to confirm and ensure the accuracy of the developed software. The calculation techniques were optimized for the analysis of the data obtained by the FSM method, which constitutes a significant part of the study. Most appropriate algorithm was determined to use the output of characterizations for recognition of materials, and the results were proved.

Several experiment setups of FSM method were used to show the interaction of the electromagnetic waveguide with the material at different angles for determination of the dielectric properties of a material. In this system, the signals, which are reflected and transmitted from the sample surface, are collected as shown in **Figure 4**. FSM method is preferred for all measurements over than 75 GHz. At other frequencies, the antennas and distances between them were changed to keep the system as reliable. In order to be able to measure in the frequency range of 75–325 GHz by FSM method, four different experimental setups were required. For this reason, antenna structures (WR10, WR8.0, WR5.1, and WR3.4) were changed, and measurements were taken in four different stages up to 325 GHz. To be able to measure up to 500 GHz (between 325 and 500 GHz), WR2.2 antenna structure must be used in the fifth stage. Measurements were made in the 75–325 GHz frequency range without using a parabolic mirror. The results of analyzed materials (Paper, Ultralam, PVC, Glass, Teflon, L1000HF, Rexolite, and RO3003) are seen in **Figure 5**. Newton-Raphson technique was used in the calculations. Lowest and highest values were entered for prediction of the algorithm instead of classic initial value assignment. Only specified (S_{21}) parameter of the materials is used for determining the complex permittivity.

For the first time, an analysis of the materials given in **Figure 5** has been made and shared in this frequency range. Due to the different measurement methods and using of different calculation techniques, little negligible differences can be obtained in the results. As the frequency band expands, the change in the dielectric constant values is not constant. For this reason, the thickness and dielectric constant values of each material are shown in **Table 2**. Ultralam, L1000HF, RO3003, and Rexolite materials measured different thicknesses as they are supplied from the manufacturer with different dimensions.



Figure 5. The dielectric constants of materials obtained by FSM method.

Material	Thickness (mm)	Dielectric constant
Paper	0.15	2.10–2.14
Ultralam	0.17	2.95–3.10
PVC	0.25	2.90-3.05
Glass	3	4.12-4.16
Teflon	4	1.98–2.05
L1000HF	3.20	9.95-10.05
Rexolite	12.85	2.52–2.55
RO3003	1.53	2.99–3.05

Table 2. Measurement of materials in W-band (75–110 GHz).

3.2. Multimode laser diode: time-domain spectroscopy (MLD-TDS) system

Various methods such as poorman's THz-TDS, Quasi-TDS (QTDS), and MLD-TDS are invented to obtain THz signal. In last two decades, the studies about multimode laser diode (MLD) that one of them can be grouped in three as THz pulse generation, sample analysis, and 2D imaging [10, 31–33]. Photoconductive antennas provide THz radiation by generating current ripple at pico-second time interval. To do this, a sudden fluctuation of the beam from the MLD is used [34, 35]. The idea of generating THz pulses from an MLD with this feature has been proposed by Hangyo. In his study, MLD-induced Photo-Conductive Antenna (PCA) is shown to be capable of producing THz pulses, and the THz pulse was measured with a bolometer that was sensitive to temperature change instead of antenna [33, 36]. In this first study, Hyodo and his colleagues used an experimental setup and added MLD instead of a dual-chip microchip laser as a beam source [36, 37]. In later researches, similar systems have been established, and obtaining THz pulses are aimed with different antenna structures. In addition, the dielectric constant and refractive index of the sample were measured to define the material [11, 34, 38].

3.2.1. Features of MLD for TDS system

Spectroscopy systems determine the response of the material to electromagnetic fields. THz-TDS system can be simply expressed in terms of production and detection of THz radiation in time domain. Two optical arms are seen in such systems in the same experimental setup as one for production and the other for detection. Ultra-fast lasers (UFL) are used as a beam source in this system. THz radiation is produced by one of the two branches of the incoming beam. THz waveform is obtained as a function of time, while the detection beam is scanned by interferometric steps. The first measurement of THz waveform is used as reference information. Spectroscopic information about the sample is obtained by examining the measurements of THz-TDS under the Fourier Transform (FD). In general, the time shift in main THz peak, the change on refractive index, and amplitude are related with power absorption of the sample [39].

MLD is proposed as an alternative cheaper and smaller beam source to design TDS systems, which are frequently used in material characterization and imaging processes [36]. The researches show that the signals obtained via MLD are like those obtained via the TDS one. THz pulse can be generated between the frequencies of 0.1–1 THz [10, 36].

PCAs are electrical components of MLD-THz spectroscopy system, and others are passive components. When the system is installed, first the passive components, then the electrical components are placed. The test setup consists of the generation and detection paths. The beam paths and system components of MLD-TDS are shown in **Figure 6**.

The working principle of the developed MLD measurement system is like the THz-TDS system. The light beam, from the MLD, is divided into two by the beam splitter. The beam, which follows the two paths known as generation and detection arms, is focused on the antennas by the objective lens. The signals emitted by the antennas are directed by parabolic mirrors. PCA, a device made of a semiconductor material, known changed the electrical conductivity when interacting with light, can convert infrared rays to THz. By exciting with



Figure 6. Schematic representation of MLD-TDS system.

laser beams focusing on the photoconductive antenna, the carriers are accelerated. Thus, the conductivity is increased and the photoaxis is created by a voltage signal from the function generator THz signal, radiating from the silicon lens face of the antenna, producing THz electric field. The relationship between the light intensity induced by the lock-in amplifier and the THz electric field is obtained as a function of the delay time. The delay time generated for the THz pulse is mechanically designed. Voltage/current values obtained from the locked amplifier are stored by LabVIEW software and plotted THz wave profile by time.

When previous researches are analyzed, only very low energy THz signals could be obtained. If the energy goes up, the nonlinear effect will decrease. However, this is an undesirable situation in MLD-TDS systems. Obtained signal should be at least 25 times of the noise. But the magnitude of obtained THz pulse by MLD is one hundredth or millionth of the magnitude of the pulsed system [15]. Therefore, the diameters of the parabolic mirrors should be large and positioned as close to the antenna as possible. The focal length of the parabolic mirror should be small, and the solid angle should be large to obtain higher signal. And of course, used antenna should be compatible with MLD-TDS systems.

3.2.2. Measurement with MLD-TDS system

The parabolic mirrors are used in the system for better collecting and aligning of generated THz signals, and the ambient conditions are most effective factors in weakening THz signal. If the focal points of the parabolic mirrors are less than 10 cm, the power of THz signal can be maintained. Since THz signals produced by MLD-TDS have very low amplitude values (Volt

or Ampere) than THz-TDS systems, the signal should align meticulously and the distance of the catheter should be short.

In the material characterization process with TDS systems, firstly, the refractive index should be calculated to determine the dielectric constant. Refractive index is given by amplitude difference between sampled and unsampled measurements in pico-seconds the shift of the THz signal. The waveform of obtained data, from w/o sample measurements of PVC sample, is seen in **Figure 7**. This spectroscopy system consists of MLD, driver, and cooler. Mostly, the softwares called Origin and Pkgraph are used for analysis. Origin was preferred for this study because of visual advantages of its interface.

Two different equations are used to calculate the refractive index depending on time and frequency. The refractive index can be obtained via Eq. 3, where Δt (s) is the shift of THz signal that is interacted with the sample. *c* and *d* represent speed of light (mm/s) and thickness of the material (mm), respectively.

$$n = \frac{c\Delta t}{2d} \tag{3}$$

$$n = \sqrt{\varepsilon_r \mu_r} \tag{4}$$

The complex permittivity (ε) of PVC was calculated by using Eq. 4 and expressed as shown in **Figure 8**. Signal degradation occurs after frequency of 0.6 THz on the measurements results obtained with MLD spectroscopy system. But signal quality is observed promising up to 0.8 THz for some material measurements. The measurement capability of the system is suitable up to about 1.2 THz, but the diagram of the signal is limited to 0.8 THz for more accurate material characterization.

Quality of THz signal obtained via MLD-TDS is not as good as ultra-short femtosecond laser source using TDS systems, but the measurement results of MLD-TDS are at least as successful



Figure 7. The measuring of PVC material by MLD-TDS system.



Figure 8. The complex permittivity of PVC sample.

as them. Researches on MLD-TDS systems are increasing because of being cheaper and more compact than THz-TDS. In this study, cheaper laser driver and cooler were used instead of conventional ones. Cooling is very important subject for MLD not to shift on mode spacing, which prevents THz signal generation, and if the limit current value to be applied to MLD is exceeded while supplying laser driver circuit, MLD will run like a standard LED emitting 808-nm laser beam.

3.3. Quasi-optical FSM method

The distance between the antennas should be kept within a certain range for generating planar wave while using FSM method. The distance between the antennas can be reduced by forming the planar waveguide at a shorter distance using the lens and parabolic mirrors. When parabolic mirrors are used to generate better THz signals and send aligning the center of the sample, the name of the system is revised as Quasi-Optical. Parabolic mirrors ensure more accurate data by focusing THz signal on the sample, and it enables to measure little-sized samples by FSM method [12]. Thus, sizing limitation problem of FSM method is already solved as seen in **Figure 9**.

Very precise adjustment is required to put parabolic mirrors since they align incoming beam. Normally, incoming beam is aligned by using infrared camera before PCA. Generated THz signal is directed to parabolic mirror, where it is aligned circular before sending next parabolic mirror. Aligning THz signal with the infrared camera is not so complicated since the wavelength of the beam is around 800 nm, but this is not so easy for FSM method. Repeat and repeat measurement may be needed while determining the position of the parabolic mirrors.

Before interpreting the results of measurements made with quasi-optical FSM method, some of mathematical approaches are needed to be clarified. When there is difficulty of generating THz signal with FSM method, highly likely expected error signals and unwanted situations should be eliminated. Some of signal correction techniques should be applied to correct the measured signals as seen below.

Measurement Methods and Extraction Techniques to Obtain the Dielectric Properties of Materials 95 http://dx.doi.org/10.5772/intechopen.80276



Figure 9. Schematic representation of quasi-optical FSM method.

Two different measurements are taken as with and without sample to perform the signal correction process, and the transmission (S_{21}) and the reflection (S_{11}) parameters are revised by considering these measurements as seen in Eq. 5 and 6, where *m*, *c*, *a*, and *l* represent material, correction, air (empty), thickness of the material, respectively, and β can be obtained via Eq. 7.

$$S_{21_c} = \frac{S_{21_m}}{S_{21_a}e^{(j\beta l)}}$$
(5)

$$S_{11_c} = \frac{S_{11_m} - S_{11_a}}{S_{21_a} e^{(j\beta l)}}$$
(6)

$$\beta = 2\pi f \sqrt{\varepsilon_0 \mu_0} \tag{7}$$

However, some filtering methods may be needed if noise and error signals still exist. In this study, measurements were made at a frequency band of 140–500 GHz. Measurements of the material up to 325 GHz can be performed by using Quasi-optical FSM correctly even repeated a few times, when the calibration is done in a proper method. But for measurement at the band of 325–500 GHz, some of noise and error signals may still exist, even though signal correction

steps have been made. The Singular Spectrum Analysis (SSA) method should be applied to remove them after using Eq. 5 and 7 as seen in **Figure 10**.

Obtained revised transmission parameter (S_{21}) is used to calculate dielectric constant of the materials as shown in **Figure 11**. The high transmission amplitude parameter of the measured materials plays a facilitating role in the measurement. The dielectric constant of PMMA is seen about 2.6 (F/m) up to frequency of 325 GHz, but it decreases to 2.55 (F/m) for higher frequencies. For PVC, it is similar with about 2.9 (F/m) up to 325 GHz and 2.87 (F/m) at the band of 325–500 GHz.



Figure 10. Corrected signal of PVC sample.



Figure 11. The results of complex permittivity obtained via quasi-optical TDS.
4. Extraction techniques

Before measurements, the study includes the calibration, which is performed to collect the correct data, and the extraction, where the dielectric properties are determined after measurements. Different calibrating techniques were applied and compared in the studies [40–42]. The most basic extraction technique Nicolson-Ross-Weir (NRW) is widely used for extracting the dielectric properties [43, 44]. Numerical methods, such as Newton-Raphson (N-R), Genetic Algorithm (GA), and Root Finding Algorithm (RFA), are used as well beside of this analytical method. Artificial neural networks (ANN) algorithms, which can be learned by analysis of obtained data from calculation, are also used in estimating the complex permittivity [45–47].

The results, obtained from analyzed data by these extraction techniques, give an approximate value to the results of the mathematical theory. By optimizing these analytical and numerical techniques, the complex permittivity and refractive index of materials can be extracted with a smaller error rate and higher accuracy. To obtain more accurate results, the extraction techniques should be compared according to the above criteria and the most suitable one should be determined. Collected data by VNA are needed to purify from errors and noise. Indeed, the accuracy of the calibration is deteriorated especially while long-term measurements. Because of the difficulties of recalibration, filtering process is preferred.

4.1. Analytical and numerical extraction techniques

Basically, the complex permittivity and permeability of the materials are extracted by reflection (S_{21}) and/or transmission (S_{11}) parameters, which are called as scattering parameters [48]. In these processes, many techniques such as Nicholson-Ross-Weir (NRW), NIST, Root Find Algorithm (RFA), and Genetic Algorithm (GA) are used [45, 49]. The techniques used in the extraction process can be divided into two main categories as analytical and numerical. Details of most preferred NRW (analytical) and Newton-Raphson (numerical) extraction techniques are given in this study.

Analytical techniques generally require precise and explicit expression. For this reason, expressions are understandable and easy to use. However, in the NRW extraction technique, the equations become unstable and erroneous at a certain interval of the sample thickness. Therefore, analytical techniques are unstable for universal computational solutions [29, 50]. An iterative extraction method is proposed for dielectric materials to come from above resonances (to remove instantaneous peaks), when the sample thickness is greater than half the wavelength [51]. Unlike analytical techniques, numerical solution techniques, which are iterative methods, cover a wide range of algorithms. The biggest disadvantage of numerical extraction techniques is that it is necessary to estimate the value to be extracted before starting the extraction methods [29, 50].

4.2. Nicolson-Ross-Weir technique

The complex permittivity extraction technique, called NRW, was developed by Nicolson, Ross, and Weir [43, 44]. In this technique, transmission (T) and reflection (Γ) coefficients are extracted by using S-parameters. The NRW extraction technique is also the basis of other

techniques as it is relatively simple among other techniques [4]. In calculations, in FSM method, the cut-off wavelength (λ_c) is expressed as infinite, and the cut-off frequency (f_c) is expressed as a value very close to zero [5].

The dielectric constant of the material (ε_r) is calculated with the NRW technique by using Sparameters measured by the Vector Network Analyzer (VNA) and following the process steps [52]. Reflection coefficient (Γ) is expressed with Eq. 8, where $|\Gamma| < 1$ is required to find correct root. Unknown X is expressed by placing S-parameters as seen on Eq. 9, and transmission coefficient (T) can be calculated by Eq. 10. Also, the expression of a special equation of the inverse triangle (capital lambda) is calculated as seen on Eq. 11.

$$\Gamma = X \mp \sqrt{X^2 - 1} \tag{8}$$

$$X = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}} \tag{9}$$

$$T = \frac{S_{11} + S_{21} - \Gamma}{1 - \Gamma(S_{11} + S_{21})}$$
(10)

$$\frac{1}{\Lambda^2} = \left(\frac{j}{2\pi d} \ln\left(T\right)\right)^2 \tag{11}$$

 λ_{og} can be calculated by using cut-off wavelength λ_c and free space wavelength λ_o as seen on Eq. 12, and the complex permittivity and permeability are calculated by Eq. 13 and 14, respectively. Eq. 8 and 9 are the basis for many analytical and numerical solutions.

$$\lambda_{\rm og} = \frac{1}{\sqrt{\frac{1}{\lambda_0^2} - \frac{1}{\lambda_c^2}}} \tag{12}$$

$$\mu^* = \frac{\lambda_{\rm og}}{\Lambda} \left(\frac{1+\Gamma}{1-\Gamma} \right) \tag{13}$$

$$\varepsilon^* = \frac{\lambda_o^2 \left(\frac{1}{\Lambda^2} + \frac{1}{\lambda_c^2}\right)}{\mu^*} \tag{14}$$

4.3. Newton-Raphson technique

Thanks to the iterative structure of the Newton-Raphson (N-R) technique, the best solution can be found. Only the transmission (S_{11}) or the reflection (S_{21}) parameter is enough to extract the complex permittivity. Normally, NRW technique requires these two parameters both for the extraction. If one of the reflection or transmission parameter is weak on measurement of the sample, N-R extraction technique should be selected [45, 49]. The transmission parameter S_{21} needs to be redefined for N-R technique as seen on Eq. 15 [21].

$$S_{21} = \frac{T(1 - \Gamma^2)}{1 - T^2 \Gamma^2}$$
(15)

Transmission (T) and Reflection (Γ) coefficients are expressing interaction between material and electromagnetic wave. If the transmission (S_{21}) parameter seen on Eq. 15 is revised for the N-R technique, real (*i*) and imaginary (*r*) parts of complex permittivity are obtained as seen on Eq. 16 and 17, respectively. Measured parameter is indexed by (*m*). Tolerance value is obtained by taking the derivatives of Eq. 16 and 17 as seen on Eq. 18.

$$\varphi(\varepsilon_r, \varepsilon_i) = S_{21_r}(\varepsilon_r, \varepsilon_i) - S_{21m_r}$$
(16)

$$\phi(\varepsilon_r, \varepsilon_i) = S_{21_i}(\varepsilon_r, \varepsilon_i) - S_{21m_i}$$
(17)

$$D = \begin{vmatrix} \left(\frac{dS_{21_r}}{d\varepsilon_r}\right) & \left(\frac{dS_{21_r}}{d\varepsilon_i}\right) \\ \left(\frac{dS_{21_i}}{d\varepsilon_r}\right) & \left(\frac{dS_{21_i}}{d\varepsilon_i}\right) \end{vmatrix}$$
(18)

And next unknown values of ε_r and ε_i can be calculated by Eq. 19 and 20, where *h* and *k* are correction for the results, and *o* is initial value. The iteration is repeated until the desired value is obtained in this technique.

$$\varepsilon_r = \varepsilon_{r_0} + h \tag{19}$$

$$\varepsilon_i = \varepsilon_{i_0} + k \tag{20}$$

4.4. Comparison of analytical and numerical techniques

It is observed that the studies using NRW technique have different algorithms. Therefore, before the comparison, it is needed to have a decision which NRW algorithm will be compared with N-R. In this study, five different NRW algorithms, which are named as NRW1, NRW2, NRW3, NRW4 and NRW5, were evaluated.

According to NRW1, cut-off wavelength (λ_c) and the cut-off frequency (f_c) are used to obtain the complex permittivity (ε) by using Eq. 21. According to NRW2, the V_1 and V_2 values are represented sum and gap of S parameters as seen on Eq. 22 and 23, and impedance (Z) can be calculated by these values as seen on Eq. 24.

$$\lambda_{\rm og} = \frac{1}{\sqrt{\frac{1}{\lambda_0^2} - \frac{1}{\lambda_{\rm c}^2}}} \tag{21}$$

$$V_1 = S_{21} + S_{11} \tag{22}$$

$$V_2 = S_{21} - S_{11} \tag{23}$$

$$Z = \frac{\sqrt{1 + V_1}\sqrt{1 - V_2}}{\sqrt{1 - V_1}\sqrt{1 + V_2}}$$
(24)

The use of S-parameters in terms of voltage sum and difference is also seen in the NRW3 algorithm. X and transmission coefficient T are calculated as seen on Eq. 25 and 26, respectively, instead of calculating impedance (Z) value.

$$X = \frac{1 - V_1 V_2}{V_1 - V_2} \tag{25}$$

$$T = \frac{V_1 - \Gamma}{1 - V_1 \Gamma} \tag{26}$$

As seen in Eq. 26, transmission coefficient *T* is calculated, which is different to Eq. 10. In NRW4 algorithm, impedance (Z) value is calculated by using transmission (S_{11}) and reflection (S_{21}) parameters directly as seen on Eq. 27.

$$Z = \frac{(S_{11} + 1)^2 - S_{21}^2}{(S_{11} - 1)^2 - S_{21}^2}$$
(27)

In NRW5, impedance (Z) value that had been calculated by a different method is used to find the transmission coefficient T as seen on Eq. 28, which is not equal to Eq. 10 and 26.

$$T = \frac{S_{21}(Z+1)}{(1-S_{11})(Z-1)}$$
(28)

As seen on these comparisons between NRW algorithms, it can be modeled with different approaches and used in material characterization. Although NRW cannot be used in the analysis of very thick materials, it is needed to demonstrate the accuracy of another technique incase used for analysis. Therefore, many studies have been compared with NRW in the literature.

The differences in NRW extraction technique (such as NRW1, NRW2, and NRW5) may also be applied to other extraction techniques. To prove this, the NRW algorithms were compared with the Newton-Raphson (N-R) results in the same way as seen above. The real and imaginary parts



Figure 12. Comparison of Newton-Raphson and NRW techniques.

of the complex permittivity were examined. The results of the best performing algorithms (NRWs and N-R) are shown at the frequency band of 20–26.5 GHz on a thickness of 2 mm Teflon sample as seen in **Figure 12** [53]. According to results, the approaches of NRW3 and NRW5 are one-to-one overlap, and therefore, the results of NRW3 were removed from the **Figure 12**.

5. Comparison of FSM and MLD-TDS measurement methods

When the literature is reviewed, generally the dielectric properties of materials are analyzed with TDS in THz frequency region above 100 GHz. In recent years, using frequencies with FSM method are increased up to 500 GHz. Obtained results by the FSM method are compared to THz-TDS in the frequency down conversion methods by some researches. In this study, the results of FSM were compared with MLD-TDS system, which is cheaper than THz-TDS method. Two different measurement methods (FSM and MLD-TDS) were compared for different materials of various thicknesses, and necessary calculations were analyzed.

The results of complex permittivity of four samples are seen in **Figure 13**. As seen on the results, the values are close to each other except for a little gap. Although the systems are different, produced THz pulses will have same frequency. But it is noticed that not only operating in different medium but also the differences of extraction techniques affect the results.

These methods are preferred by various applications because of noncontact and nondestructive measurement possibilities, even they have different working principles. Before having a decision, which method is better, the subjects mentioned in **Table 3** and the measurement results should be considered as well.

The FSM method is disadvantageous to TDS because it requires a very expensive device such as the Vector Network Analyzer (VNA). In TDS method, cheaper laser diodes are used instead of expensive laser sources. FSM setup is simpler, because of having fewer components, and installation and testing measurement accuracy of TDS system take longer time. But performing broadband measurement with TDS is possible at one time contrary to FSM.

Due to antenna designs and productions are classified according to specific wave lengths, more than one antenna set is needed for wide band measurement or the measurement must be limited in a certain frequency band. For this reason, the discrete measurement is a limitation for FSM method.

FSM is advantageous when measuring length is concerned. Once the calibration process has been completed, the transmitted and reflected signals can be measured within seconds. But it is not possible for TDS. Only one w/o sample measurement takes 15 minutes. Though some displacement slider designs, which can measure 60 times per second, is pushed on the market to recover this, the price is needed to consider.

The stability of TDS method is adversely affected by the large number of components in the system. In addition, even if the system is protected in a housing, micron size displacement over time can cause to change laser beam path. In this case, the accuracy of measurement cannot be survived. From time to time, calibration or re-installation of measurement system may be



Figure 13. Comparison of complex permittivity with two different systems.

	FSM	MLD-TDS
Measurement frequency	Discrete	Wide
Installation length	Short	Long
Measurement length	Short	Long
Calculation length	Long	Long
System devices	Few	Many
Stability	Good	Not bad
Sensitivity	Good	Medium
Cost	Expensive	Cheap

Table 3. Comparison of FSM and MLD-TDS methods.

needed. In FSM method, even if there is any adjustment malfunction, the measurement can be continued by performing the calibration in a short time.

Comparisons made in this study are important in confirming that the results are obtained by using FSM method recently in THz frequency domain measurements. Although the

bandwidth is narrow, FSM has a good spectral resolution and dynamic range around 0.3 THz. The real parts of the complex permittivity values obtained by both methods are overlapped, but the results of the TDS system are better for the imaginary parts, probably because of multiple reflections effect in FSM. In TDS, measurements below 100 GHz, which are already outside the THz frequency domain, are not within the desired range due to the poor signal-to-noise ratio, and they are generally not shared. The measurement methods both have advantages in certain directions, and so they may be selected to use up to needs and priorities of the measurement will be done. FSM can provide more accurate results for the measurements in a certain frequency range, but TDS system can be offered for a wider frequency range as most efficient solution. These methods of measurement, thanks to developing technology, are being optimized for medical, biology, food, security, military, and other subjects to offer solutions to the problems.

6. Conclusion

In this chapter, measurement methods and extraction techniques used in material characterization are examined, and new materials were measured to show the accuracy and contribution of the proposed extraction techniques. The results of two different measurement methods with advantages relative to each other were compared, and approximate values were obtained as well as previously published studies. Thus, the usability of the FSM method in the THz frequency range has been shown using the results. Despite some disadvantages, TDS system, which uses the MLD as a light source, is more preferable than the FSM because it has a broadband spectrum measurement capability.

S-parameters collected during material measurement process were used to extract the dielectric properties with various extraction techniques, and successful results were obtained. By using Nicolson-Ross-Weir (NRW) method, which is the most basic calculation technique, various algorithms are compared and the Newton-Raphson approach which is the numerical analysis method is verified.

It must be provided that the generated THz signal is collimated to interact well with the material. In this context, the parabolic mirror, which is an optical component, can be preferred in order to efficiently use the FSM method in the THz frequency range. Due to the optical component used in the measurement method, the new system is called optical-like FSM. Due to the advantage of this system, hybrid systems consisting of optical and microwave measurement methods in the frequency range of 0.5–1 THz are predicted to be used more widely in the future.

Acknowledgements

We would like to thank to Osamu Morikawa (Chair of Liberal Arts, Japan Coast Guard Academy, Kure, Japan) for his supports.

Author details

Turgut Ozturk^{1*} and Muhammet Tahir Güneşer²

*Address all correspondence to: turgutozturk@karabuk.edu.tr

- 1 Department of Electrical-Electronics Engineering, Karabuk University, Turkey
- 2 Department of Electrical-Electronics Engineering, Bursa Technical University, Turkey

References

- [1] Skocik P, Neumann P. Measurement of complex permittivity in free space. Procedia Engineering. 2015;**100**:100-104. DOI: 10.1016/j.proeng.2015.01.347
- [2] Rajesh Mohan RM, Mridula S, Mohanan P. Study and analysis of dielectric behavior of fertilized soil at microwave frequency. EJAET. 2015;2:73-79
- [3] Nelson SO. Measurement of microwave dielectric properties of particulate materials. Journal of Food Engineering. 1994;**21**:365-384. DOI: 10.1016/0260-8774(94)90080-9
- [4] Rocha LS, Junqueira CC, Gambin E, Nata Vicente A, Culhaoglu AE, Kemptner E. A free space measurement approach for dielectric material characterization. In: SBMO/IEEE MTT-S International Microwave and Optoelectronics Conference. IEEE; 2013. pp. 1-5. DOI: 10.1109/IMOC.2013.6646474
- [5] Tereshchenko OV, Buesink FJK, Leferink FBJ. An overview of the techniques for measuring the dielectric properties of materials. In: XXXth URSI General Assembly and Scientific Symposium. IEEE; 2011. pp. 1-4. DOI: 10.1109/URSIGASS.2011.6050287
- [6] Jilani MT, Zaka M, Khan AM, Khan MT, Ali SM. A brief review of measuring techniques for characterization of dielectric materials. International Journal of Information Technology and Electrical Engineering. 2012;1:1-5
- [7] Ghodgaonkar DK, Varadan VV, Varadan VK. Free-space measurement of complex permittivity and complex permeability of magnetic materials at microwave frequencies. IEEE Transactions on Instrumentation and Measurement. 1990;39:387-394. DOI: 10.1109/19.52520
- [8] Petersson LER, Smith GS. An estimate of the error caused by the plane-wave approximation in free-space dielectric measurement systems. IEEE Transactions on Antennas and Propagation. 2002;50:878-887. DOI: 10.1109/TAP.2002.1017671
- [9] Ozturk T, Morikawa O, Ünal İ, Uluer İ. Comparison of free space measurement using a vector network Analyzer and low-cost-type THz-TDS measurement methods between 75 and 325 GHz. Journal of Infrared, Millimeter, and Terahertz Waves. 2017;38:1241-1251. DOI: 10.1007/s10762-017-0410-1
- [10] Scheller M, Koch M. Terahertz quasi time domain spectroscopy. Optics Express. 2009;17: 17723. DOI: 10.1364/OE.17.017723

- [11] Morikawa O, Tonouchi M, Hangyo M. Sub-THz spectroscopic system using a multimode laser diode and photoconductive antenna. Applied Physics Letters. 1999;75:3772. DOI: 10.1063/1.125451
- [12] Ozturk T, Hudlička M, Uluer İ. Development of measurement and extraction technique of complex permittivity using transmission parameter S21 for Millimeter wave frequencies. Journal of Infrared, Millimeter, and Terahertz Waves. 2017;38:1510-1520. DOI: 10.1007/ s10762-017-0421-y
- [13] Ozturk T, Elhawil A, Uluer İ, Tahir M. Development of extraction techniques for dielectric constant from free-space measured S-parameters between 50 and 170 GHz. Journal of Materials Science: Materials in Electronics. 2017:1-7. DOI: 10.1007/s10854-017-6953-z
- [14] Narayan RM, Vu KT. Free-space microwave measurement of low moisture content in powdered foods. Journal of Food Processing & Preservation. 2000;24:39-56. DOI: 10.1111/ j.1745-4549.2000.tb00404.x
- [15] Kim KB, Park SG, Kim JY, Kim JH, Lee CJ, Kim MS, et al. Measurement of moisture content in powdered food using microwave free-space transmission technique. Key Engineering Materials. 2006;**321**:1196-1200. DOI: 10.4028/www.scientific.net/KEM.321-323.1196
- [16] Kraszewski A, Trabelsi S, Nelson S. Comparison of density-independent expressions for moisture content determination in wheat at microwave frequencies. Journal of Agricultural Engineering Research. 1998;71:227-237. DOI: 10.1006/jaer.1998.0320
- [17] Mohan RR, Paul B, Mridula S, Mohanan P. Measurement of soil moisture content at microwave frequencies. Procedia Computer Science. 2015;46:1238-1245. DOI: 10.1016/j. procs.2015.01.040
- [18] Wee FH, Soh PJ, Suhaizal AH, Nornikman H, Ezanuddin AA. Free space measurement technique on dielectric properties of agricultural residues at microwave frequencies. In: International Microwave and Optoelectronics Conference. IEEE; 2009. pp. 183-187. DOI: 10.1109/IMOC.2009.5427603
- [19] Chen LF, Ong CK, Neo CP, Varadan VV, Varadan VK. Microwave Electronics. 1st ed. Chichester, UK: John Wiley & Sons, Ltd; 2004. DOI: 10.1002/0470020466
- [20] Al-Mously SIY. A modified complex permittivity measurement technique at microwave frequency. International Journal of New Computer Architectures and Their Applications. 2012;2:389-401
- [21] Puthukodan S, Dadrasnia E, Vinod VKT, Lamela Rivera H, Ducournau G, Lampin J-F. Optical properties of carbon nanotube thin films in subterahertz frequency regime. Microwave and Optical Technology Letters. 2014;56:1895-1898. DOI: 10.1002/mop.28477
- [22] Kazemipour A, Hudlicka M, Yee S-K, Salhi MA, Allal D, Kleine-Ostmann T, et al. Design and calibration of a compact quasi-optical system for material characterization in Millimeter/Submillimeter wave domain. IEEE Transactions on Instrumentation and Measurement. 2015;64:1438-1445. DOI: 10.1109/TIM.2014.2376115

- [23] Akhtar MJ, Spiliotis NG, Omar AS. An experimental setup for the microwave imaging of inhomogeneous dielectric bodies. In: IEEE Antennas and Propagation Society International Symposium. IEEE; 2004. pp. 225-228. DOI: 10.1109/APS.2004.1329607
- [24] Ozturk T, Uluer İ, Ünal İ. Materials classification by partial least squares using Sparameters. Journal of Materials Science: Materials in Electronics. 2016;27:12701-12706. DOI: 10.1007/s10854-016-5404-6
- [25] Zhang J, Nakhkash M, Huang Y. Electromagnetic imaging of layered building materials. Measurement Science and Technology. 2001;12:1147-1152. DOI: 10.1088/0957-0233/12/8/322
- [26] Friedsam GL, Biebl EM. A broadband free-space dielectric properties measurement system at millimeter wavelengths. In: 20th Bienn. Conf. Precis. Electromagn. Meas. IEEE; 1997. pp. 210-211. DOI: 10.1109/CPEM.1996.546779
- [27] Yin H-C, Chao Z-M, Xu Y-P. A new free-space method for measurement of electromagnetic parameters of biaxial materials at microwave frequencies. Microwave and Optical Technology Letters. 2005;46:72-78. DOI: 10.1002/mop.20905
- [28] Ghodgaonkar DK, Varadan VV, Varadan VK. A free-space method for measurement of dielectric constants and loss tangents at microwave frequencies. IEEE Transactions on Instrumentation and Measurement. 1989;38:789-793. DOI: 10.1109/19.32194
- [29] Grignon R, Afsar MN, Wang Y, Butt S. Microwave broadband free-space complex dielectric permittivity measurements on low loss solids. In: 20th IEEE Instrumentation Technology Conference. IEEE; 2003. pp. 865-870. DOI: 10.1109/IMTC.2003.1208278
- [30] Ajami A, Akkara-Aketalin T, Shakhtour H, Heberling D. Experimental investigations of accuracy improvement and limitations of a free space measurement system including thin lenses. In: 7th European Conference on Antennas and Propagation. 2013. pp. 4064-4067
- [31] Scheller M, Koch M. Multi-mode continuous wave terahertz systems-quasi time domain spectroscopy. Conference on Lasers Electro-Optics. 2010;1:2-3
- [32] Scheller M, Dürrschmidt SF, Stecher M, Koch M. Terahertz quasi-time-domain spectroscopy imaging. Applied Optics. 2011;50:1884. DOI: 10.1364/AO.50.001884
- [33] Hangyo M. Development and versatile applications of terahertz time-domain spectroscopy. In: 39th International Conference on Infrared, Millimeter, Terahertz Waves. IEEE; 2014. pp. 1-4. DOI: 10.1109/IRMMW-THz.2014.6955988
- [34] Tani M, Morikawa O, Matsuura S, Hangyo M. Generation of terahertz radiation by photomixing with dual- and multiple-mode lasers. Semiconductor Science and Technology. 2005;20:S151-S163. DOI: 10.1088/0268-1242/20/7/005
- [35] Morikawa O, Fujita M, Takano K, Hangyo M. Sub-terahertz spectroscopic system using a continuous-wave broad-area laser diode and a spatial filter. Journal of Applied Physics. 2011;110:063107. DOI: 10.1063/1.3639296

- [36] Tani M, Matsuura S, Sakai K, Hangyo M. Multiple-frequency generation of sub-terahertz radiation by multimode LD excitation of photoconductive antenna. IEEE Microwave and Guided Wave Letters. 1997;7:282-284. DOI: 10.1109/75.622540
- [37] Hyodo M, Tani M, Matsuura S, Onodera N, Sakai K. Generation of millimetre-wave radiation using a dual-longitudinal-mode microchip laser. Electronics Letters. 1996;32: 1589. DOI: 10.1049/el:19961041
- [38] Morikawa O, Tonouchi M, Tani M, Sakai K, Hangyo M. Sub-THz emission properties of photoconductive antennas excited with multimode laser diode. Japanese Journal of Applied Physics. 1999;38:1388-1389. DOI: 10.1143/JJAP.38.1388
- [39] Zhang X-C, Xu J. Introduction to THzWave Photonics; 2010
- [40] Rolfes I, Schiek B. Calibration methods for microwave free space measurements. Advances in Radio Science. 2005;2:19-25. DOI: 10.5194/ars-2-19-2004
- [41] Bartley PG, Begley SB. A new free-space calibration technique for materials measurement. In: IEEE International Instrumentation and Measurement Technology Conference. IEEE; 2012. pp. 47-51. DOI: 10.1109/I2MTC.2012.6229351
- [42] Will B, Rolfes I. Application of the thru-network-line self-calibration method for free space material characterizations. In: Proceedings of 2012 International Conference on Electromagnetic Advanced Applications. ICEAA'12. 2012. pp. 831-834. DOI: 10.1109/ICEAA.2012.6328749
- [43] Nicolson AM, Ross GF. Measurement of the intrinsic properties of materials by timedomain techniques. IEEE Transactions on Instrumentation and Measurement. 1970;19: 377-382. DOI: 10.1109/TIM.1970.4313932
- [44] Weir WB. Automatic measurement of complex dielectric constant and permeability at microwave frequencies. Proceedings of the IEEE. 1974;62:33-36. DOI: 10.1109/PROC.1974.9382
- [45] Elhawil A, Vounckx R, Zhang L, Koers G, Stiens J. Comparison between two optimisation algorithms to compute the complex permittivity of dielectric multilayer structures using a free-space quasi-optical method in W-band. IET Science, Measurement and Technology. 2009;3:13-21. DOI: 10.1049/iet-smt:20070085
- [46] Liang C, Li L, Zhai H. Low-cost free-space measurement of dielectric constant at Ka band. IEE Proceedings: Microwaves, Antennas and Propagation. 2004;151:271-276. DOI: 10.1049/ip-map
- [47] Jurado A, Escot D, Poyatos D, Montiel I. Application of artificial neural networks to complex dielectric constant estimation from free-space measurements. In: Methods Model. Artif. Nat. Comput. 2009. pp. 517-526. DOI: 10.1007/978-3-642-02264-7_53
- [48] Zivkovic I, Murk A. Extraction of dielectric and magnetic properties of carbonyl iron powder composites at high frequencies. Journal of Applied Physics. 2012;111. DOI: 10.1063/1.4725473
- [49] Elhawil A, Koers G, Zhang L, Stiens J, Vounckx R. Reliable method for material characterisation using quasi-optical free-space measurement in W-band. IET Science, Measurement and Technology. 2009;3:39-50. DOI: 10.1049/iet-smt:20070086

- [50] Gagnon N, Shaker J, Berini P, Roy L, Petosa A. Correction and extraction techniques for dielectric constant determination using a Ka-band free-space measurement system. In: 32nd European Microwave Conference 2002. IEEE; 2002. pp. 1-4. DOI: 10.1109/EUMA.2002.339410
- [51] Baker-Jarvis J, Jones C, Riddle B, Janezic M, Geyer RG, Grosvenor JH, et al. Dielectric and magnetic measurements: A survey of nondestructive, quasi-nondestructive, and processcontrol techniques. Research in Nondestructive Evaluation. 1995;7:117-136. DOI: 10.1007/ BF02538826
- [52] Rutpralom T, Chamnongthai K, Kumhom P, Krairiksh M. Nondestructive durian maturity determination by using microwave free space measurement. In: IEEE International Symposium on Circuits & Systems. IEEE; 2006. pp. 1351-1354. DOI: 10.1109/ISCAS.2006.1692844
- [53] Ozturk T, Elhawil A, Düğenci M, Ünal İ, Uluer İ. Extracting the dielectric constant of materials using ABC-based ANNs and NRW algorithms. Journal of Electromagnetic Waves and Applications. 2016;30:1785-1799. DOI: 10.1080/09205071.2016.1215266



Edited by Md. Kawsar Alam

Materials properties, whether microscopic or macroscopic, are of immense interest to the materials scientists, physicists, chemists as well as to engineers. Investigation of such properties, theoretically and experimentally, has been one of the fundamental research directions for many years that has also resulted in the discovery of many novel materials. It is also equally important to correctly model and measure these materials properties. Keeping such interests of research communities in mind, this book has been written on the properties of polyesters, varistor ceramics, and powdered porous compacts and also covers some measurement and parameter extraction methods for dielectric materials. Four contributed chapters and an introductory chapter from the editor explain each class of materials with practical examples.

Published in London, UK © 2019 IntechOpen © FactoryTh / iStock

IntechOpen

