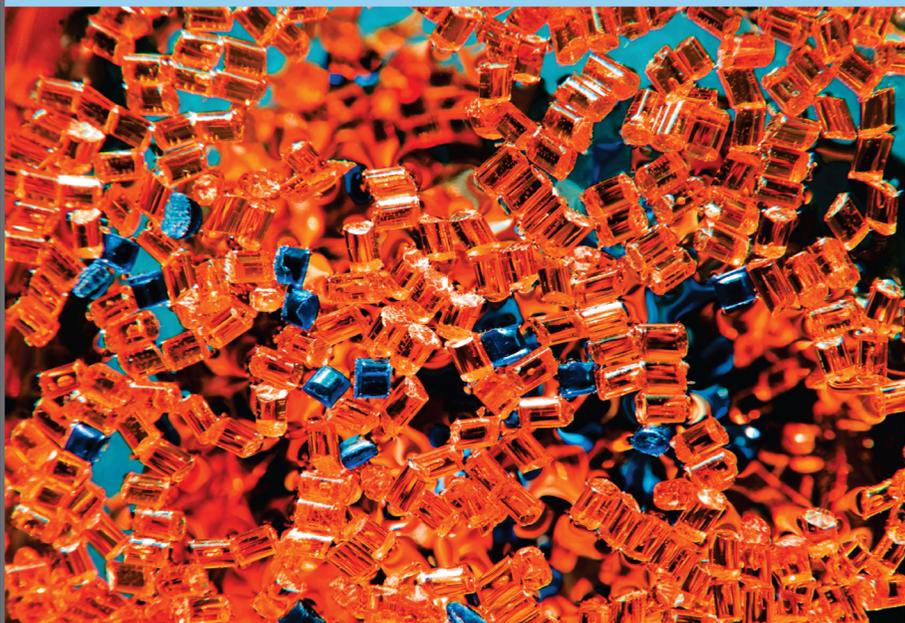


Nanomaterials and Nanotechnology for Composites

Design, Simulation, and Applications



Editors

A. K. Haghi, PhD • Sabu Thomas, PhD
Ali Pourhashemi, PhD • Abbas Hamrang, PhD
Ewa Kłodzińska, PhD

AAP | APPLE
ACADEMIC
PRESS

CRC | CRC Press
Taylor & Francis Group

NANOMATERIALS AND NANOTECHNOLOGY FOR COMPOSITES

Design, Simulation, and Applications

This page intentionally left blank

NANOMATERIALS AND NANOTECHNOLOGY FOR COMPOSITES

Design, Simulation, and Applications

Edited by

**A. K. Haghi, PhD, Sabu Thomas, PhD,
Ali Pourhashemi, PhD, Abbas Hamrang, PhD, and
Ewa Kłodzińska, PhD**

AAP | APPLE
ACADEMIC
PRESS

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Apple Academic Press, Inc
3333 Mistwell Crescent
Oakville, ON L6L 0A2
Canada

© 2015 by Apple Academic Press, Inc.

Exclusive worldwide distribution by CRC Press an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works
Version Date: 20150429

International Standard Book Number-13: 978-1-4822-6387-9 (eBook - PDF)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

For information about Apple Academic Press product
<http://www.appleacademicpress.com>

ABOUT THE EDITORS

A. K. Haghi, PhD

A. K. Haghi, PhD, holds a BSc in urban and environmental engineering from the University of North Carolina (USA); a MSc in mechanical engineering from North Carolina A&T State University (USA); a DEA in applied mechanics, acoustics and materials from Université de Technologie de Compiègne (France); and a PhD in engineering sciences from Université de Franche-Comté (France). He is the author and editor of 165 books and has published 1000 research papers in various journals and conference proceedings. Dr. Haghi has received several grants, consulted for a number of major corporations, and is a frequent speaker to national and international audiences. Since 1983, he served as a professor at several universities. He is currently Editor-in-Chief of the *International Journal of Chemoinformatics and Chemical Engineering* and *Polymers Research Journal* and on the editorial boards of many international journals. He is a member of the Canadian Research and Development Center of Sciences and Cultures (CRDCSC), Montreal, Quebec, Canada.

Sabu Thomas, PhD

Dr. Sabu Thomas is the Director of the School of Chemical Sciences, Mahatma Gandhi University, Kottayam, India. He is also Professor of polymer science and engineering and the Director of the International and Inter University Centre for Nanoscience and Nanotechnology of the same university. He is a fellow of many professional bodies. Professor Thomas has authored or coauthored many papers in international peer-reviewed journals in the area of polymer processing. He has organized several international conferences and has more than 420 publications, 11 books, and two patents to his credit. He has been involved in a number of books both as author and editor. He is a reviewer to many international journals and has received many awards for his excellent work in polymer processing. His h Index is 42. Professor Thomas is listed as the 5th position in the list of Most Productive Researchers in India, in 2008.

Ali Pourhashemi, PhD

Ali Pourhashemi, PhD, is currently Professor of chemical and biochemical engineering at Christian Brothers University (CBU) in Memphis, Tennessee. He was formerly the Department Chair at CBU and also taught at Howard University in Washington, DC, USA. He taught various courses in chemical engineering, and his main area has been teaching the capstone process design as well as supervising industrial internship projects. He is a member of several professional organiza-

tions, including the *American Institute of Chemical Engineers*. He is on the international editorial review board of the *International Journal of Chemoinformatics and Chemical Engineering* and is an editorial member of the *International of Journal of Advanced Packaging Technology*. He has published many articles and presented at many professional conferences.

Abbas Hamrang, PhD

Abbas Hamrang, PhD, is Professor of polymer science and technology. He is currently a senior Polymer Consultant and Editor and member of the academic board of various international journals. His research interests include degradation studies of historical objects and archival materials, cellulose-based plastics, thermogravimetric analysis, accelerated aging process, and stabilization of polymers by chemical and nonchemical methods. His previous involvement in academic and industry sectors at international level include deputy vice-chancellor of research & development, senior lecturer, manufacturing consultant, science and technology advisor.

Ewa Kłodzińska, PhD

Ewa Kłodzińska holds a PhD from Nicolaus Copernicus University, Faculty of Chemistry in Torun, Poland. For 10 years, she has been doing research on determination and identification of microorganisms using the electromigration techniques for the purposes of medical diagnosis. Currently she is working at the Institute for Engineering of Polymer Materials and Dyes and investigates surface characteristics of biodegradable polymer material on the basis of zeta potential measurements. She has written several original articles, monographs, and chapters in books for graduate students and scientists. She has made valuable contributions to the theory and practice of electromigration techniques, chromatography, sample preparation, and application of separation science in pharmaceutical and medical analysis. Dr. Ewa Kłodzińska is a member of editorial board of *ISRN Analytical Chemistry* and the *International Journal of Chemoinformatics and Chemical Engineering (IJCCE)*.

CONTENTS

<i>List of Contributors</i>	<i>ix</i>
<i>List of Abbreviations</i>	<i>xiii</i>
<i>List of Symbols</i>	<i>xvii</i>
<i>Preface</i>	<i>xxi</i>
1. Influence of a Strong Electric Field on the Electrical, Transport and Diffusion Properties of Carbon Nanostructures with Point Defects Structure	1
S. A. Sudorgin and N. G. Lebedev	
2. Carbon-Polymer Nanocomposites with Polyethylene as a Binder: A Research Note	15
Sergei V. Kolesov, Marina V. Bazunova, Elena I. Kulish, Denis R. Valiev, and Gennady E. Zaikov	
3. Application of Polymers Containing Silicon Nanoparticles as Effective UV Protectors	25
A. A. Olkhov, M. A. Goldshtrakh, and G. E. Zaikov	
4. Dynamically Vulcanized Thermoelastoplastics Based on Butadiene-Acrylonitrile Rubber and Polypropylene Modified Nanofiller	39
S. I. Volfson, G. E. Zaikov, N. A. Okhotina, A. I. Nigmatullina, O. A. Panfilova, and A. A. Nikiforov	
5. Sorption Active Carbon Polymer Nanocomposites: A Research Note	47
Marina Bazunova, Rustam Tukhvatullin, Denis Valiev, Elena Kulish, and Gennadij Zaikov	
6. Modification of Physical and Mechanical Properties of Fiber Reinforced Concrete Using Nanoparticles	59
M. Mehdipour	
7. UV-Protective Nanocomposites Films Based on Polyethylene	73
A. A. Olkhov, M. A. Goldshtrakh, G. Nyszko, K. Majewski, J. Pielichowski, and G. E. Zaikov	
8. Nanocomposite Foils Based On Silicate Precursor with Surface Active Compounds: A Research Note	87
L. O. Zaskokina, V. V. Osipova, Y. G. Galyametdinov, and A. A. Momzyakov	

9. Experimental Investigation on the Effects of Nano Clay on Mechanical Properties of Aged Asphalt Mixture.....	93
M. Arabani, A. K. Haghi, and R. Tanzadeh	
10. Nanostructural Elements and the Molecular Mechanics and Dynamics Interactions: A Systematic Study.....	107
A. V. Vakhrushev and A. M. Lipanov	
11. A Study on Biological Application of Ag and Co/Ag Nanoparticles Cytotoxicity and Genotoxicity	139
Iman E. Gomaa, Samarth Bhatt, Thomas Liehr, Mona Bakr, and Tarek A. El-Tayeb	
12. The Transfer Variants of Metal/Carbon Nanocomposites Influence on Liquid Media: A Research Note	155
V. I. Kodolov and V. V. Trineeva	
13. Analysis of the Metal/Carbon Nanocomposites Surface Energy: A Research Note	163
V. I. Kodolov and V. V. Trineeva	
14. Nanopolymer Fibers: A Very Comprehensive Review in Axial and Coaxial Electrospinning Process.....	171
Saeedeh Rafiei and A. K. Haghi	
15. A Study on Polymer/Organoclay Nanocomposites	351
K. S. Dibirova, G. V. Kozlov, and G. M. Magomedov	
16. A Very Detailed Review on Application of Nanofibers in Energy and Environmental	359
Saeedeh Rafiei, Babak Noroozi, and A. K. Haghi	
Index.....	419

LIST OF CONTRIBUTORS

M. Arabani

Professor, Faculty of Engineering, University of Guilan, Rasht, Postal code: 3756, I. R. Iran; Tel: +98(131)6690270; Fax: +98 (131) 6690270; E-mail: arabani@guilan.ac.ir

Mona Bakr

The National Institute for Laser Enhanced Sciences, Cairo University, Egypt

Marina V. Bazunova

Scientific Degree: The Candidate of the Chemical Sciences. Post: The Docent of the Department of High-Molecular Connections and General Chemical Technology of the Chemistry Faculty of the Bashkir State University; Official Add: 450076, Ufa, Zaks Validi Street, 32; Tel.: (347) 229-96-86; Mob: 89276388192; E-mail: mbazunova@mail.ru

Samarth Bhatt

Jena University Hospital, Friedrich Schiller University, Institute of Human Genetics, Kollegiengasse 10, D-07743 Jena, Germany

K. S. Dibirova

Dagestan State Pedagogical University, Makhachkala 367003, Yaragskii Street 57, Russian Federation

Tarek A. El-Tayeb

The National Institute for Laser Enhanced Sciences, Cairo University, Egypt

Y. G. Galyametdinov

Doctor of Chemical Sciences, Head of Department of Physical and Colloid Chemistry, KNRTU; E-mail: office@kstu.ru

M. A. Goldshtrakh

Military Institute of Chemistry and Radiometry, 105 Allea of General A. Chrusciela, 00-910 Warsaw, Poland, M. V. Lomonosov State University of Fine Chemical Technology, 119571 Moscow, Vernadskogo prosp 86

Iman E. Gomaa

German University in Cairo, Egypt, Main Entrance of Al-Tagamoa Al-Khames; E-mail: iman.gomaa@guc.edu.eg; Tel: +20-0100 2155053; Fax: +20-2-27590772

A. K. Haghi

Professor, Faculty of Engineering, University of Guilan, Rasht, Postal code: 3756, I. R. Iran; Tel: +98(131)6690270; Fax: +98 (131) 6690270; E-mail: Haghi@guilan.ac.ir

V. I. Kodolov

Basic Research High Educational Centre of Chemical Physics & Mesoscopy, Udmurt Scientific Centre, Ural Division; Russian Academy of Sciences, M. T. Kalashnikov Izhevsk State Technical University

Sergei V. Kolesov

Scientific Degree: The Doctor of the Chemical Sciences. Post: The Professor of the Department of High-Molecular Connections and General Chemical Technology of the Chemistry Faculty of the Bashkir State University; Official add: 450076 Ufa, Zaks Validi Street, 32; Tel.: (347) 229-96-86; E-mail: Kolesovservic@mail.Ru

G. V. Kozlov

Dagestan State Pedagogical University, Makhachkala 367003, Yaragskii Street 57, Russian Federation

Elena I. Kulish

Scientific Degree: The Doctor of the Chemical Sciences. Post: The Professor of the Department of High-Molecular Connections and General Chemical Technology of the Chemistry Faculty of the Bashkir State University. Official add: 450076, Ufa, Zaks Validi Street 32; Tel.: (347) 229-96-86; E-mail: Onlyalena@mail.Ru

N. G. Lebedev

Volgograd State University, Volgograd, Russia; E-mail: lebedev.ng@mail.ru

Thomas Liehr

Jena University Hospital, Friedrich Schiller University, Institute of Human Genetics, Kollegiengasse 10, D-07743 Jena, Germany

A. M. Lipanov

Institute of Mechanics, Ural Branch of the Russian Academy of Sciences, T. Baramsinoy 34, Izhevsk, Russia; E-mail: postmaster@ntm.udm.ru

G. M. Magomedov

Dagestan State Pedagogical University, Makhachkala 367003, Yaragskii Street 57, Russian Federation

K. Majewski

Military Institute of Chemistry and Radiometry, 105 Allee of General A. Chrusciela, 00-910 Warsaw, Poland; E-mail: K.Majewski@wichir.waw.pl

M. Mehdipour

Textile Engineering Department, Guilan University, Rasht, Iran

A. I. Nigmatullina

Chemistry and Processing Technology of Elastomers Department, Kazan National Research Technological University, 68 K Marks street, Kazan, Russia; E-mail: Chembio@sky.chph.ras.ru

A. A. Nikiforov

Chemistry and Processing Technology of Elastomers Department, Kazan National Research Technological University, 68K Marks street Kazan, Russia; E-mail: Chembio@sky.chph.ras.ru

Babak Noroozi

Department of Textile Engineering, University of Guilan, P. O. Box 41635-3756, Rasht, Iran

G. Nyszko

Military Institute of Chemistry and Radiometry, 105 Allee of General A. Chrusciela, 00-910 Warsaw, Poland, E-mail: Grzegorz.Nyszko@wichir.waw.pl

N. A. Okhotina

Chemistry and Processing Technology of Elastomers Department, Kazan National Research Technological University, 68 K Marks street Kazan, Russia; E-mail: Chembio@sky.chph.ras.ru

A. A. Olkhov

N. N. Semenov Institute of Chemical physics Russian Academy of Sciences, 119991 Moscow, street Kosygina, 4; E-mail: aolkhov72@yandex.ru

V. V. Osipova

Ph. D. Department of Physical and Colloid Chemistry, KNRTU

O. A. Panfilova

Chemistry and Processing Technology of Elastomers Department, Kazan National Research Technological University, 68K Marks street, Kazan, Russia, E-mail: Chembio@sky.chph.ras.ru

J. Pielichowski

Cracow University of Technology, Department of Polymer Science and Technology, Warszawska street, 31-155 Krakow, Poland, E-mail: Pielich@pk.edu.pl

Saeedeh Rafiei

Department of Textile Engineering, University of Guilan, P.O. Box 41635-3756, Rasht, Iran

S. A. Sudorgin

Volgograd State University, Volgograd, Russia, Volgograd State Technical University, Volgograd, Russia; E-mail: sersud@mail.ru

R. Tanzadeh

Department of Civil Engineering University of Guilan, Rasht, Iran. Tel: +98(131)3229883; Fax: +98 (131) 3231116; E-mail: rashidanzadeh@yahoo.com

V. V. Trineeva

Basic Research High Educational Centre of Chemical Physics & Mesoscopy, Udmurt Scientific Centre, Ural Division; Russian Academy of Sciences, Institute of Mechanics, Ural Division, Russian Academy of Sciences

Rustam Tukhvatullin

Bashkir State University, 32 Zaki Validi Street, 450076 Ufa, Republic of Bashkortostan, Russia

A. V. Vakhrushev

Institute of Mechanics, Ural Branch of the Russian Academy of Sciences, T. Baramsinoy 34, Izhevsk, Russia; E-mail: postmaster@ntm.udm.ru

Denis R. Valiev

Scientific Degree:-Post: The Student of the Department of High-Molecular Connections and General Chemical Technology of the Chemistry Faculty of the Bashkir State University Official add: 450076, Ufa, Zaks Validi Street, 32; Tel. Official: (347) 229-96-86; E-mail: valief@mail.ru

S. I. Volfson

Chemistry and Processing Technology of Elastomers Department, Kazan National Research Technological University, 68K Marks street, Kazan, Russia; E-mail: Chembio@sky.chph.ras.ru

Gennady E. Zaikov

Institute of Biochemical Physics named N. M. Emanuel of Russian Academy of Sciences Scientific Degree: The Doctor of the Chemical Sciences; Official add: 4 Kosygina Street, 119334, Moscow, Russia; E-mail: chembio@sky.chph.ras.ru

L. O. Zaskokina

Master of Department of Physical and Colloid Chemistry, KNRTU

This page intentionally left blank

LIST OF ABBREVIATIONS

AC	Activated Carbon
ACF	Activated Carbon Fibers
ACHF	Activated Carbon Hollow Fibers
ACNF	Activated Carbon Nanofiber
AFM	Atomic Force Microscope
AN	Acrylonitrile
BEM	Boundary Element Method
BET	Brunner-Emmett1-Teller
BGK	Bhatnagar-Gross-Krook
BJH	Barrett Joiner Halenda
BSA	Bovine Serum Albumin
CF	Carbon Fiber
CFD	Computational Fluid Dynamics
CH	Calcium Hydroxide
CNT	Carbon Nanotubes
CS	Cellulose
CVD	Chemical Vapor Deposition
DAAD	Deutsche Akademische Austausch Dienst
DDT	Dichlorodiphenyltrichloroethane
DMF	Dimethylformamide
DSB	Double Strand Breaks
EDLCs	Electrochemical Double-Layer Capacitors
EDXS	Energy Dispersive X-Ray Spectrometry
EELS	Electron Energy Loss Spectroscopy
EMEM	Eagle's Minimal Essential Medium
ERKs	Extracellular Signal-Regulated Kinases
FEM	Finite Element Methods
FRC	Fiber-Reinforced Concrete
FTIR	Fourier Transform Infrared
GUC	German University in Cairo
HDPE	High Density Polyethylene
HTS	High Temperature Shearing
HTT	Heat-Treatment Temperature
ISCN	International System for human Cytogenetic Nomenclature
ITZ	Interfacial Transition Zone

LBM	Lattice Boltzmann methods
LDPE	Low Density Polyethylene
LED	Light Emitting Diode
LERT	Large Electrical Relaxation Time Limit
LIBs	Lithium-Ion Batteries
MA	Maleine Anhydride
MD	Molecular Dynamics
MFCs	Microbial Fuel Cells
MMA	Methyl Methacrylate
MWNTs	Multiwall Carbon Nanotubes
NDT	Nottingham Device Test
NEMs	Nano-Electro-Mechanical Systems
NF	Nanofiltration
NILES	National Institute of Laser Enhanced Sciences
NPs	Nanoparticles
NS	Nano-SiO ₂
NT	Nano-TiO ₂
ODE's	Ordinary Differential Equations
PAA	Poly (Acrylic Acid)
PAN	Polyacrylonitrile
PBS	Phosphate Buffer Saline
PCN	Polymer Clay Nanocomposites
PDEs	Partial Differential Equations
PEM	Proton Exchange Mat
PGA	Poly(Glycolic Acid)
PHEV	Plug-In Hybrid Electric Vehicles
PLLA	Poly (L-Lactic Acid)
PMMA	Poly(Methyl Methacrylate)
POM	Polarization Optical Microscopy
PP	Polypropylene
PPX	Poly (P-Xylylene)
PTT	Photo Thermal Therapy
PVDC	Polyvinylidene Chloride
PZT	Plumbum Zirconate Titanate
RF	Radio-Frequency
RNP	Responsive Nanoparticle
RSM	Response Surface Methodology
RVE	Representative Volume Element
SAN	Styrene-Co-Acrylonitrile
SBS	Styrene-Butadiene-Styrene
SEI	Solid Electrolyte Interphase
SEM	Scanning Electron Microscope

SERT	Small Electrical Relaxation Time Limit
SMPE	Sulfophenyl Methallyl Ether
SSB	Single Strand Breaks
SSS	Sodium P-Styrene Sulfonate
SWNTs	Single Wall Carbon Nanotubes
TEM	Transmission Electron Microscopy
TFOT	Thin Film Oven Test
TG	Thermogravimetric Method
THF	Tetrahydrofuran
TLBM	Thermal Lattice Boltzmann methods
VA	Vinyl Acetate
VOCs	Volatile Organic Compounds

This page intentionally left blank

LIST OF SYMBOLS

A_m	amplitude of nanocomposite vibration
A_{ms}	coefficients of Fourier expansion
b	width of the Specimen
c	velocity of light
d	density of the adsorbate, g/cm^3
$\langle d \rangle_V$	average arithmetic size
d_f	fractal dimension
\bar{F}_{max}	maximal force
$\bar{\mathbf{F}}_c$	principal vector of forces
$f_c(p, r)$	Fermi distribution function
$ \bar{\mathbf{F}}_{bi} $	force magnitude of the nanoparticle interaction
$\bar{\mathbf{F}}_i(t)$	random set of forces at a given temperature
L	span length
\bar{l}	mean segment length
M	mass of the dried sample
$\bar{\mathbf{M}}_c$	principal moment
Me (d)	median of distribution defining the size d
Mo (d)	position of maximum (a distribution mode)
m_i	mass of the i^{th} atom
m	mass of adsorbed benzene
$m_{\text{absorbed water}}$	mass of the water
m_{av}	average mass of medium
m_{cl}	mass of metal containing phase
m_{sample}	mass of the sample
N	number of carbon atoms in lattice
N_{imp}	number of adsorbed hydrogen atoms
N_k	number of atoms forming each nanoparticle
n	number of interatomic interaction types
P	maximum indicated load
p_x	parallel component of the graphene sheet
q	charge of ion
R	flexural strength
S'	modulus of elasticity
S''	loss modulus
s	quasimomentum of the electrons in grapheme

$T(r)$	constant in the linear approximation in magnitude
U	constant of Coulomb repulsion of impurity
U_{trans}	electromagnetic wave transmission velocity
V	hybridization potential
\vec{V}_{i0}, \vec{V}_i	initial and current velocities
V_{lj}	matrix element of hybridization

GREEK CHARACTERS

α_{am}	amorphous phase relative fraction
α_i	friction coefficient in atomic structure
$c_{j\sigma}$	Fermi annihilation
$c_{j\sigma}^+$	creation operators of electrons
ϵ_{ab}	absolute dielectric constant for medium
$\epsilon_{\text{s}}^{\text{prog}}$	nanocomposite surface energy portion
$\epsilon_{\text{s}}^{\text{NC}}$	surface energy of nanocomposite
$\mathcal{E}_{l\sigma}$	energy of electron by impurity
Ω_k	area occupied by nanoelement
Φ_{cb}	chemical bonds
Φ_{es}	electrostatics
Φ_{pg}	flat groups
Φ_{hb}	hydrogen bonds
$\Phi(\vec{\rho}_{ij})$	potential depending on mutual positions of all atoms
$\vec{\rho}_{ij}$	radius vector determining the position of the i^{th} atom relative to the j^{th} atom
Φ_{ta}	torsion angles
Φ_{va}	valence angles
Φ_{vv}	Vander Waals contacts
λ	wave length
$n_{l\sigma}^d$	number of electrons on impurities
ρ	medium density
$\vec{\rho}_{cj}$	vector connecting points c and j
g	axial viscous normal stress
χ	relative fraction of elastically deformed polymer
$y(j,l)$	length distribution
t_{Δ}	electron hopping integral
U_{ζ}	velocity vector of the interface
μ_{ab}	absolute magnetic penetrability of medium
Φ_{m}	maximum potential of electromagnetic radiation of nanocomposite
\vec{x}_{i0}, \vec{x}_i	original and current coordinates

σ_Y	yield stress
ν	Poisson's ratio
n_F	Flory exponent

This page intentionally left blank

PREFACE

Engineered nanopolymer and nanoparticles, with their extraordinary mechanical and unique electronic properties, have garnered much attention in the recent years. With a broad range of potential applications, including nanoelectronics, composites, chemical sensors, biosensors, microscopy, nanoelectromechanical systems, and many more, the scientific community is more motivated than ever to move beyond basic properties and explore the real issues associated with carbon nanotube-based applications.

Engineered nanopolymer and nanoparticles are exceptionally interesting from a fundamental research point of view. They open up new perspectives for various applications, such as nano-transistors in circuits, field-emission displays, artificial muscles, or added reinforcements in alloys. This text is an introduction to the physical concepts needed for investigating carbon nanotubes and other one-dimensional solid-state systems. Written for a wide scientific readership, each chapter consists of an instructive approach to the topic and sustainable ideas for solutions.

A large part of the research currently being conducted in the fields of materials science and engineering mechanics is devoted to Engineered nanopolymer and nanoparticles and their applications. In this process, modeling is a very attractive investigation tool due to the difficulties in manufacturing and testing of nanomaterials. Continuum modeling offers significant advantages over atomistic modeling. Furthermore, the lack of accuracy in continuum methods can be overtaken by incorporating input data either from experiments or atomistic methods. This book reviews the recent progress in application of Engineered nanopolymer and nanoparticles and their composites. The advantages and disadvantages of different methods are discussed. The ability of continuum methods to bridge different scales is emphasized. Recommendations for future research are given by focusing on what each method has to learn from the nano-scale. The scope of the book is to provide current knowledge aiming to support researchers entering the scientific area of carbon nanotubes to choose the appropriate modeling tool for accomplishing their study and place their efforts to further improve continuum methods.

This page intentionally left blank

CHAPTER 1

INFLUENCE OF A STRONG ELECTRIC FIELD ON THE ELECTRICAL, TRANSPORT AND DIFFUSION PROPERTIES OF CARBON NANOSTRUCTURES WITH POINT DEFECTS STRUCTURE

S. A. SUDORGIN^{1,2} and N. G. LEBEDEV¹

¹Volgograd State University, Volgograd, Russia

²Volgograd State Technical University, Volgograd, Russia

E-mail: sergsud@mail.ru, lebedev.ng@mail.ru

CONTENTS

Abstract.....	2
1.1 Introduction.....	2
1.2 Model and Basic Relations	3
1.3 Results and Discussion	6
1.4 Conclusion	12
Keywords	12
References.....	12

ABSTRACT

Examines the influence of defects on the electrical properties of carbon nanostructures in an external electric field. Defects are the hydrogen atoms, which adsorbed on the surface of carbon nanostructures. Carbon nanostructures are considered the single-walled “zigzag” carbon nanotubes Atomic adsorption model of hydrogen on the surface of single-walled “zigzag” carbon nanotubes based on the single-impurity Anderson periodic model. Theoretical calculation of the electron diffusion coefficient and the conductivity of “zigzag” carbon nanotubes alloy hydrogen atoms carried out in the relaxation time approximation. Revealed a decrease in the electrical conductivity and the electron diffusion coefficient with increasing concentration of adsorbed hydrogen atoms. The nonlinearity of the electrical conductivity and the diffusion coefficient of the amplitude of a constant strong electric field at the constant concentration of hydrogen adatoms shown at the figures.

This work was supported by the Russian Foundation for Basic Research (grant № 13–03–97108, grant № 14–02–31801), and the Volgograd State University grant (project № 82–2013-a/VolGU).

1.1 INTRODUCTION

Despite the already long history of the discovery of carbon nanotubes (CNT) [1], the interest in the problem of obtaining carbon nanostructures with desired characteristics unabated, constantly improving their synthesis. Unique physical and chemical properties of CNTs can be applied in various fields of modern technology, electronics, materials science, chemistry and medicine [2]. One of the most important from the point of view of practical applications is the transport property of CNTs.

Under normal conditions, any solid surfaces coated with films of atoms or molecules adsorbed from the environment, or left on the surface in the diffusion process [3]. The most of elements adsorption on metals forms a chemical bond. The high reactivity of the surface of carbon nanotubes makes them an exception. Therefore, current interest is the study of the influence of the adsorption of atoms and various chemical elements and molecules on the electrical properties of carbon nanostructures.

In the theory of adsorption, in addition to the methods of quantum chemistry, widely used the method of model Hamiltonians [3]. In the study of the adsorption of atoms and molecules on metals used primarily molecular orbital approach – self-consistent field, as this takes into account the delocalization of electrons in the metal. Under this approach, the most commonly used model Hamiltonian Anderson [4, 5], originally proposed for the description of the electronic states of impurity atoms in the metal alloys. The model has been successfully applied to study the adsorption of atoms on the surface of metals and semiconductors [6], the adsorption of hydrogen on the surface of graphene [7] and carbon nanotubes [8, 9].

In this chapter, we consider the influence of the adsorption of atomic hydrogen on the conducting and diffusion properties of single-walled “zigzag” CNTs. Interaction of hydrogen atoms adsorbed to the surface of carbon nanotubes is described in terms of the periodic Anderson model. Since the geometry of the CNT determines their conductive properties, then to describe the adsorption on the surface of CNTs using this model is justified. Transport coefficients (conductivity and diffusion coefficient) CNT electron calculated by solving the Boltzmann equation [10] in the relaxation time approximation.

This technique was successfully applied by authors to calculate the ideal transport characteristics of carbon nanotubes [11], graphene bilayer graphene [12] and graphene nanoribbons [13].

1.2 MODEL AND BASIC RELATIONS

However, with the discovery of new forms of carbon model can be successfully applied to study of the statistical properties of CNTs and graphene. Carbon atom in the nanotube forms three chemical connection σ -type. Lodging with nearest neighbor atoms with three- sp^2 hybridization of atomic orbitals. The fourth p -orbital involved in chemical bonding π -type which creates π -shell nanotube describing state of itinerant electrons, that define the basic properties of CNTs and graphene. This allows us to consider the state of π -electron system in the framework of the Anderson model. The model takes into account the kinetic energy of electrons and their Coulomb interaction at one site and neglected energy inner-shell electrons of atoms and electrons involved in the formation of chemical bonds σ -type, as well as the vibrational energy of the atoms of the crystal lattice.

In general, the periodic Anderson model [5] considers two groups of electrons: itinerant s -electrons and localized d -electrons. Itinerant particles are considered free and localized – interact by Coulomb repulsion on a single node. With the discovery of new forms of carbon model can be successfully applied to study the statistical properties of carbon structures are the CNT and the graphene. Carbon atom in the graphene layer has three forms chemical bonds σ -type with its immediate neighbors. The fourth orbital p -type forms a chemical bond π -type, describing the state of itinerant electrons. States localized electrons created by the valence orbitals (in this case, the p -type) impurity atoms. This allows us to consider the state of π -electrons in the framework of the Anderson model. The model takes into account the kinetic energy of the electrons in the crystal and impurity electrons interacting through a potential hybridization, and neglects the energy of the electrons of the inner shells of atoms and electrons involved in the formation of chemical bonds σ -type, as well as the vibrational energy of the atoms of the crystal lattice [5].

In the periodic Anderson model state of the electrons of the crystal containing impurities in the π -electron approximation and the nearest neighbor approximation is described by the effective Hamiltonian, having the following standard form [5]:

$$\begin{aligned}
H = \sum_{j,\Delta,\sigma} t_{\Delta} \left(c_{j\sigma}^+ c_{j+\Delta\sigma} + c_{j+\Delta\sigma}^+ c_{j\sigma} \right) + \sum_{l,\sigma} \varepsilon_{l\sigma} n_{l\sigma}^d + \sum_l U n_{l\uparrow}^d n_{l\downarrow}^d + \\
+ \sum_{l,j,\sigma} \left(V_{lj} c_{j\sigma}^+ d_{l\sigma} + V_{lj}^* d_{l\sigma}^+ c_{j\sigma} \right)
\end{aligned} \quad (1)$$

where t_{Δ} is the electron hopping integral between the neighboring lattice sites of the crystal; U is the constant of the Coulomb repulsion of the impurity; $c_{j\sigma}$ and $c_{j\sigma}^+$ are the Fermi annihilation and creation operators of electrons in the crystal node j with spin σ ; $d_{j\sigma}$ and $d_{j\sigma}^+$ are the Fermi annihilation and creation operators of electrons on the impurities l with spin σ ; $n_{l\sigma}^d$ is the operator of the number of electrons on impurities l with spin σ ; $\varepsilon_{l\sigma}$ is the energy of the electron by the impurity l with spin σ ; V_{lj} is the matrix element of hybridization of impurity electron l and atom j of the crystal.

After the transition to k -space by varying the crystal by Fourier transformation of creation and annihilation of electrons and crystal use the Green function method, the band structure of single-walled CNTs with impurities adsorbed hydrogen atoms takes the form [8, 9]:

$$E(\mathbf{k}) = \frac{1}{2} \left[\varepsilon_k + \varepsilon_{l\sigma} \pm \left((\varepsilon_k - \varepsilon_{l\sigma})^2 + 4 \frac{N_{imp}}{N} |V|^2 \right)^{\frac{1}{2}} \right], \quad (2)$$

where N – number of carbon atoms in the lattice, determines the size of the crystal, N_{imp} – the number of adsorbed hydrogen atoms, V – hybridization potential, $\varepsilon_{l\sigma} = -5.72$ eV – electron energy impurities – the band structure of an ideal single-walled nanotubes, for tubes, for example, “zigzag” type dispersion relation is defined as follows [1]:

$$E(\mathbf{p}) = \pm \gamma \sqrt{1 + 4 \cos(ap_x) \cos(\pi s / n) + 4 \cos^2(\pi s / n)} \quad (3)$$

where $a = 3d / 2\hbar$, $d = 0.142$ nm is the distance between adjacent carbon atoms in graphene, $\mathbf{p} = (p_x, s)$ is the quasimomentum of the electrons in graphene, p_x is the parallel component of the graphene sheet of the quasimomentum and $s = 1, 2, \dots, n$ are the quantization numbers of the momentum components depending on the width of the graphene ribbon. Different signs are related to the conductivity band and to the valence band accordingly.

Used in the calculation of the Hamiltonian parameters: the value of the hopping integral $t_0 = 2.7$ eV, hybridization potential $V = -1.43$ eV estimated from quantum chemical calculations of the electronic structure of CNTs within the semiempirical MNDO [14]. Electron energy impurity $\varepsilon_{l\sigma} = -5.72$ eV was assessed using the method described in Refs. [6, 7].

Consider the effect of the adsorption of atomic hydrogen on the response of single-walled “zigzag” CNTs to an external electric field applied along the x -axis is directed along the axis of the CNT (Fig. 1.1).

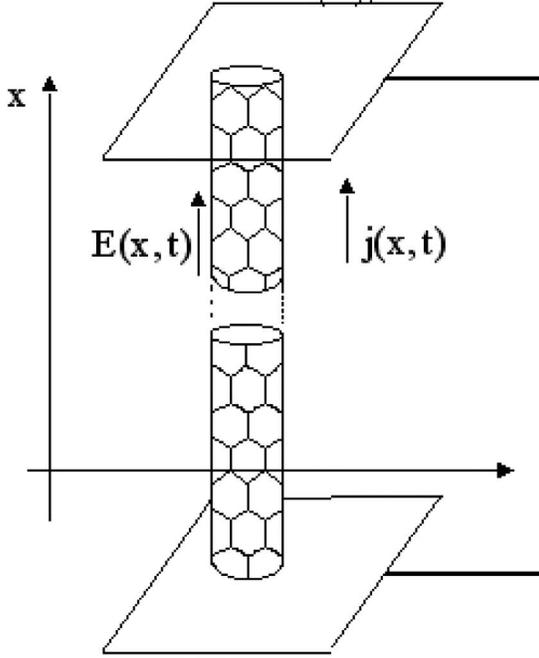


FIGURE 1.1 Geometry configuration. CNT type “zigzag” is in an external electric field. Field strength vector \mathbf{E} is directed along the axis of the CNT.

Method of calculating the transport coefficients of electrons in carbon nanotubes described in detail in Refs. [11–13]. Evolution of the electronic system was simulated in the semiclassical approximation of the relaxation time. Electron distribution function in the state with momentum $p = (p_x, s)$ is of the t – approximation using Boltzmann equation [10]:

$$\frac{\partial f_s(\mathbf{p}, \mathbf{r})}{\partial t} + \mathbf{F} \frac{\partial f_s(\mathbf{p}, \mathbf{r})}{\partial \mathbf{p}} = \frac{f_s(\mathbf{p}, \mathbf{r}) - f_{0s}(\mathbf{p}, \mathbf{r})}{\tau}, \quad (4)$$

where $f_s(\mathbf{p}, \mathbf{r})$ – the Fermi distribution function $\mathbf{F} = e\mathbf{E}$ – acting on the particle constant electrostatic force.

To determine the dependence of the diffusion and conductive characteristics of CNTs on the external electric field using the procedure outlined in Ref. [15]. The longitudinal component of the current density $j = j_x$ has the following form:

$$j(x) = \sigma(\mathbf{E})\mathbf{E} + D(\mathbf{E})\frac{\nabla_x n}{n} \quad (5)$$

For the case of a homogeneous temperature distribution $T(r) = \text{const}$ in the linear approximation in magnitude [11], expressions for the transport coefficients of single-walled nanotubes: conductivity and diffusivity of electrons. Electrical conductivity of CNT type “zigzag” given following expression [11]:

$$\sigma(E) = \sum_s \int_{-\pi}^{\pi} \sum_m A_{ms} m f_{0s}(p_x, x) \frac{E}{E^2 m^2 + 1} [\sin(mp_x) + Em \cos(mp_x)] dp_x \quad (6)$$

Expression for the diffusion coefficient of electrons in CNT type “zigzag” has the form [11]:

$$D(E) = \sum_s \int_{-\pi}^{\pi} f_{0s}(p_x, x) \sum_m A_{ms} m \sum_{m'} A_{m's} m' \left\{ \frac{[E^2(m^2 + m'^2) + 1][EmR + M]}{K} + \frac{[E^3(m'^3 - 2m^2 m') + Em']T}{K} \right\} dp_x + \sum_s \int_{-\pi}^{\pi} f_{0s}(p_x, x) \sum_m A_{ms} m \sum_{m'} A_{m's} m' \frac{F}{P} dp_x, \quad (7)$$

where the following notation:

$$K = [E^4(m^4 + m'^4 - 2m^2 m'^2) + 2E^2(m^2 + m'^2) + 1][E^2 m^2 + 1]$$

$$P = [E^2 m^2 + 1]^2 [E^2 m'^2 + 1]$$

$$R = \cos(mp_x) \sin(m'p_x) + \cos(mp_x) \cos(m'p_x) - \sin(mp_x) \sin(m'p_x)$$

$$M = \sin(mp_x) \sin(m'p_x) + \sin(mp_x) \cos(m'p_x) + \cos(mp_x) \sin(m'p_x)$$

$$T = [\cos(mp_x) \cos(m'p_x) - Em \sin(mp_x) \cos(m'p_x)]$$

$$F = [\sin(m'p_x) + Em \cos(m'p_x)][\sin(mp_x) + 2Em \cos(mp_x) - E^2 m^2 \sin(mp_x)]$$

$A_{ms}, A_{m's}$ are the coefficients of the Fourier expansion of the dispersion relation of electrons in CNT, m and m' order Fourier series. For the convenience of visualization and qualitative analysis performed procedure and select the following dimensionless relative unit of measurement of the electric field $E0 = 4.7 \times 10^6$ V/m.

1.3 RESULTS AND DISCUSSION

To investigate the influence of an external constant electric field on the transport properties of single-walled CNT type “zigzag” with adsorbed hydrogen atoms

selected the following system parameters: temperature $T \approx 300$ K, the relaxation time is $\tau \approx 10^{-12}$ s in accordance with the data [16]. For numerical analysis considered type semiconducting CNT (10,0).

It should be noted that a wide range of external field behavior of the specific conductivity $\sigma(E)$ for nanotubes with hydrogen adatoms has the same qualitative nonlinear dependence as for the ideal case of nanoparticles, which was discussed in detail in Ref. [11]. In general, the dependence of conductivity on the electric field has a characteristic for semiconductors form tends to saturate and decreases monotonically with increasing intensity. This phenomenon is associated with an increase in electrons fill all possible states of the conduction band. Behavior of electrical conductivity under the influence of an external electric field is typical for semiconductor structures with periodic and limited dispersion law [17].

Figure 1.2 shows the dependence of conductivity $\sigma(E)$ on the intensity of the external electric field E for ideal CNT (10,0) and CNT (10,0) with adsorbed hydrogen atom at relatively low fields. The graphs show that the addition of single adsorbed atom (adatom) hydrogen reduces the conductivity by a small amount (about 2×10^{-3} S/m). Lowering the conductivity of the hydrogen atom in the adsorption takes place due to the fact that one of the localized electron crystallite forms a chemical bond with the impurity atom and no longer participates in the charge transport by CNT.

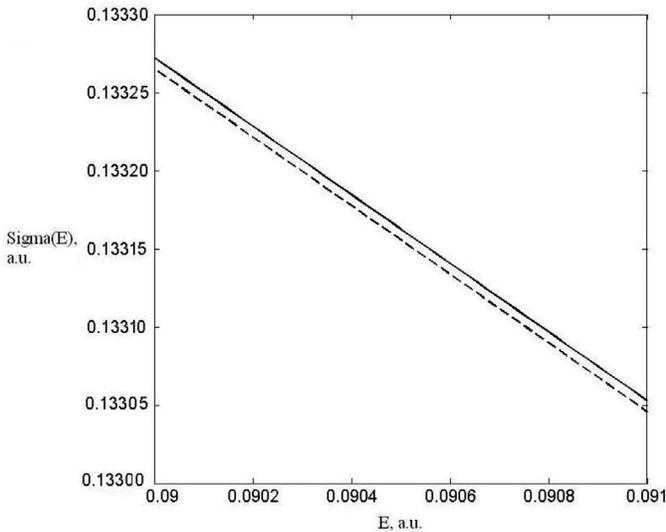


FIGURE 1.2 Dependence of the conductivity $\sigma(E)$ on the magnitude of tension external electric field E : for ideal CNT (10,0) – solid line and the CNT (10,0) with hydrogen adatom – dashed line. x -axis is a dimensionless quantity of the external electric field E (unit corresponds to 4.7×10^6 V/m), the y -axis is dimensionless conductivity $\sigma(E)$ (unit corresponds to 1.9×10^3 S/m).

Also analyzed the dependence of the conductivity $\sigma(E)$ on the intensity of the external electric E for CNT (10,0) type, containing different concentrations of hydrogen adatoms (Fig. 1.3). The increasing of the number of adsorbed atoms reduces the conductivity of “zigzag” CNT proportional to the number of localized adsorption bonds formed. When you add one hydrogen adatom conductivity of CNT type (10,0) is reduced by 0.06%, adding 100 adatoms by 0.55%, adding 300 adatoms by 1.66%, adding 500 adatoms by 2.62%.

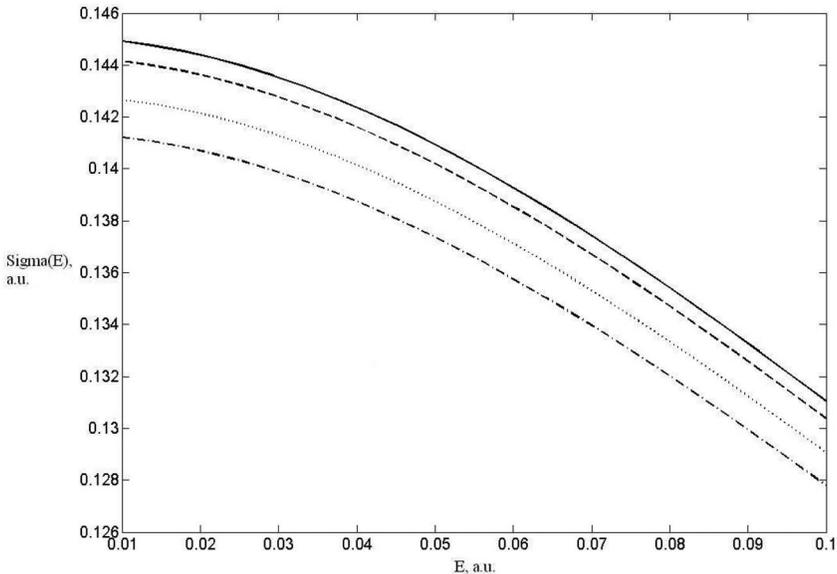


FIGURE 1.3 Dependence of the conductivity $\sigma(E)$ on the magnitude of tension E external electric impurity for CNT (10,0) one hydrogen adatom – solid line; 100 adatoms – dashed line; 300 adatoms – dotted line; 500 adatoms – dash-dot line. x -axis is a dimensionless quantity of the external electric field E (unit corresponds to 4.7×10^6 V/m), the y -axis is dimensionless conductivity $\sigma(E)$ (unit corresponds to 1.9×10^3 S/m).

Figure 1.4 shows that this behavior is typical for semiconductor conductivity of CNTs with different diameters. With the increasing diameter of the nanotubes have high electrical conductivity, since they contain a larger amount of electrons, which may participate in the transfer of electrical charge. The graphs in Fig. 1.4 shows for the (5,0), (10,0) and (20,0) CNT with the addition of 100 hydrogen adatoms.

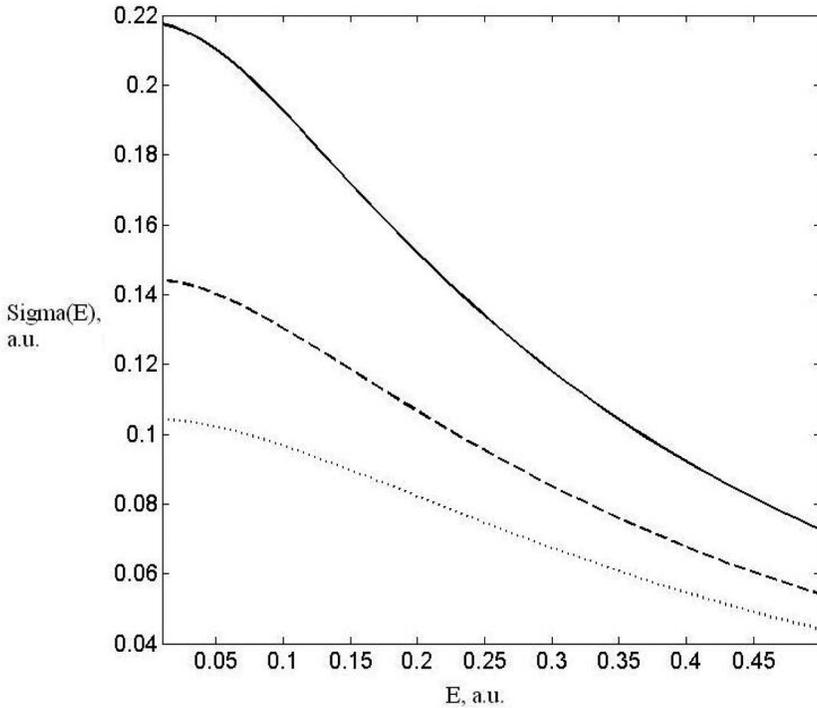


FIGURE 1.4 Dependence of the conductivity $\sigma(E)$ on the magnitude of tension external electric E for different types of CNTs with the addition of hydrogen adatoms 100 (20,0) – solid line, (10,0) – dashed line; (5,0) – the dotted line. x -axis is a dimensionless quantity of the external electric field E (unit corresponds to 4.7×10^6 V/m), the y -axis is dimensionless conductivity $\sigma(E)$ (unit corresponds to 1.9×10^3 S/m).

The electron diffusion coefficient $D(E)$ from the electric field in the single-walled “zigzag” CNT with adsorbed hydrogen atoms has a pronounced nonlinear character (Fig. 1.5). Increase of the field leads to an increase in first rate, and then to his descending to a stationary value. This phenomenon is observed for all systems with intermittent and limited electron dispersion law [17]. Electron diffusion coefficient can be considered constant in the order field amplitudes $E \approx 5 \times 10^6$ V/m. The maximum value of the diffusion coefficient for semiconductor CNTs observed at field strengths of the order of $E \approx 4.8 \times 10^5$ V/m.

When adding the adsorbed hydrogen atoms the electron diffusion coefficient, as well as the conductivity is reduced by 0.05% (Fig. 1.5). This behavior of the diffusion coefficient in an external electric field is observed for different concentrations

of hydrogen adatoms (Fig. 1.6) and semiconductor CNTs with different diameters by adding 100 adatoms (Fig. 1.7).

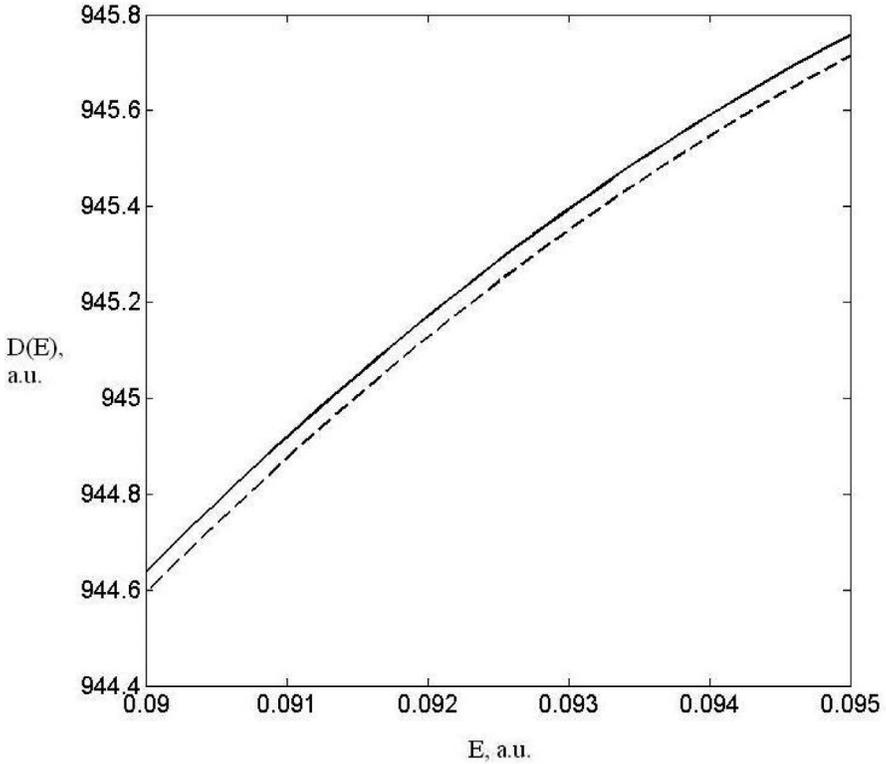


FIGURE 1.5 Dependence of the electron diffusion coefficient $D(E)$ on the intensity of the external electric field E : for CNT (10,0) ideal – solid line and hydrogen adatom – dashed line. x -axis is a dimensionless quantity of the external electric field E (unit corresponds to 4.7×10^6 V/m), the y -axis is a dimensionless diffusion coefficient $D(E)$ (unit corresponds to 3.5×10^2 A/m).

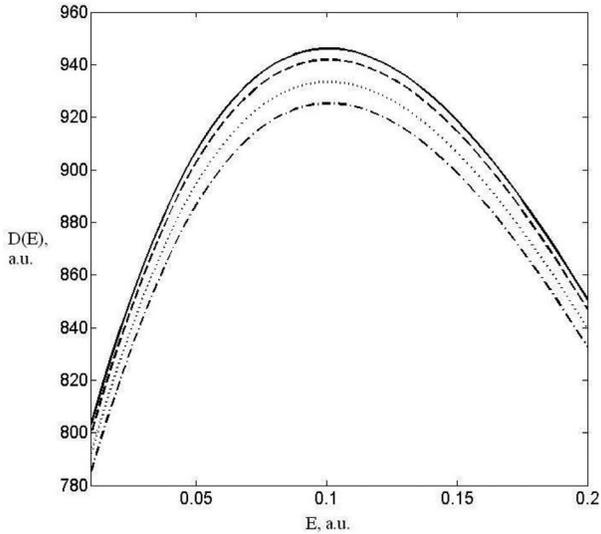


FIGURE 1.6 Dependence of the electron diffusion coefficient $D(E)$ on the intensity of the external electric E for impurity CNT (10,0) one hydrogen adatom – solid line; 100 adatoms – dashed line; 300 adatoms – dotted line; 500 adatoms – dash-dot line. x -axis is a dimensionless quantity of the external electric field E (unit corresponds to 4.7×10^6 V/m), the y -axis is a dimensionless diffusion coefficient $D(E)$ (unit corresponds to 3.5×10^2 A/m).

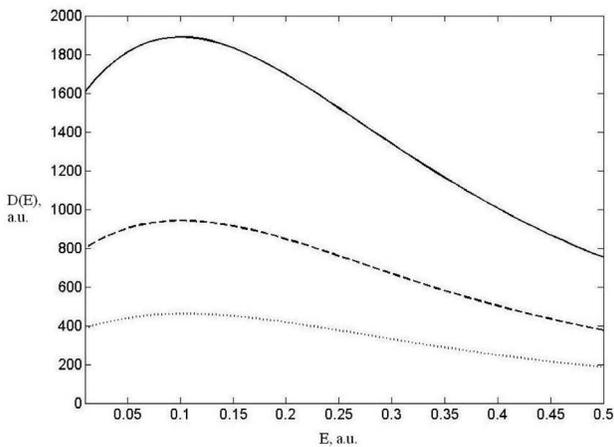


FIGURE 1.7 Dependence of the electron diffusion coefficient $D(E)$ on the intensity of the external electric E for different types of CNTs with the addition of hydrogen adatoms 100 (20,0) – solid line, (10,0) – dashed line; (5,0) – the dotted line. x -axis is a dimensionless quantity of the external electric field E (unit corresponds to 4.7×10^6 V/m), the y -axis is a dimensionless diffusion coefficient $D(E)$ (unit corresponds to 3.5×10^2 A/m).

The presented results can be used for the preparation of carbon nanotubes with desired transport characteristics and to develop the microelectronic devices, which based on carbon nanoparticles.

1.4 CONCLUSION

We formulate the main results in the conclusion.

1. The method for theoretical calculation of the semiconducting “zigzag” CNT transport properties with adsorbed hydrogen atoms developed. Analytical expressions for the conductivity and the electron diffusion coefficient in “zigzag” CNT with hydrogen adatoms in the presence of an electric field.
2. Numerical calculations showed nonlinear dependence of the transport coefficients on the electric field. For strong fields coefficients tend to saturate.
3. Atomic hydrogen adsorption of the semiconducting “zigzag” CNT reduces their conductivity by several percent. The electron diffusion coefficient also decreases with increasing concentration of adsorbed hydrogen atoms, and a decrease of the diffusion coefficient is more pronounced than the decrease of electrical conductivity for each of the above types of semiconducting CNTs at a larger number of adatoms.
4. Transport properties of nanotubes with adatoms increases with the diameter. A physical explanation for the observed effect.

KEYWORDS

- **adsorption**
- **carbon nanostructures**
- **conductivity**
- **diffusion coefficient**
- **“zigzag” nanotubes**

REFERENCES

1. Diachkov, P. N. (2010). *Electronic Properties and Applications of Nanotubes* M. Bin, the Laboratory of Knowledge, 488p.
2. Roco, M. C., Williams, R. S., & Alivisatos, A. P. (2002). *Nanotechnology in the Next Decade Forecast the Direction of Research* Springer-Verlag, 292p.
3. Bolshov, L. A., Napartovich, A. P., Naumovets, A. G., & Fedorus, A. G. (1977). *UFN T 122(1)*, S. 125.
4. Anderson, P. W. (1961). *Phys Rev. 124*, 41.

5. Izyumov, A., Chashchin, I. I., & Alekseev, D. S. (2006). The Theory of Strongly Correlated Systems Generating functional method Moscow-Izhevsk: NITs "Regular and Chaotic Dynamics" 384.
6. Davydov, S. U., & Troshin, S. V. (2007). *Phys. T.* 49 (8), S. 1508.
7. Davydov, S. Y., & Sabirov, G. I. (2010). *Letters ZHTF T.* 36(24), S. 77.
8. Pak, A. V., & Lebedev, N. G. (2012). *Chemical Physics*, 31(3), 82–87.
9. Pak, A. V., & Lebedev, N. G. (2013). *ZhFKh T.* 87, S 994.
10. Landau, L. D., & Lifshitz, E. M. (1979). *Physical Kinetics M. Sci. Lit* 528 c.
11. Belonenko, M. B., Lebedev, N. G., & Sudorgin, S. A. (2011). *Phys. T.* 53, S. 1841.
12. Belonenko, M. B., Lebedev, N. G., & Sudorgin, S. A. (2012). *Technical Physics*, 82(7), 129–133.
13. Sudorgin, S. A., Belonenko, M. B., & Lebedev, N. G. (2013). *Physical Script*, 87(1), 015602(1–4).
14. Stepanov, N. F. (2001). *Quantum Mechanics and Quantum Chemistry* Springer, Verlag, 519 sec.
15. Buligin, A. S., Shmeliov, G. M., & Maglevannaya, I. I. (1999). *Phys. T.* 41, S. 1314.
16. Maksimenko, S. A., & Slepyan, G. Ya. (2004). *Nano Electromagnetic of Low-Dimensional Structure in Handbook of Nanotechnology Nanometer Structure: Theory, Modeling, and Simulation*. Bellingham: SPIE Press, 145p.
17. Dykman, I. M., & Tomchuk, P. M. (1981). *Transport Phenomena and Fluctuations in Semiconductors*. Kiev. Science, Dumka, 320c.

This page intentionally left blank

CHAPTER 2

CARBON-POLYMER NANOCOMPOSITES WITH POLYETHYLENE AS A BINDER: A RESEARCH NOTE

SERGEI V. KOLESOV, MARINA V. BAZUNOVA, ELENA I. KULISH,
DENIS R. VALIEV, and GENNADY E. ZAIKOV

CONTENTS

Abstract.....	16
2.1 Introduction.....	16
2.2 Experimental Part.....	17
2.3 Results and Discussion	18
2.4 Conclusions.....	22
Keywords	22
References.....	22

ABSTRACT

A new approach of obtaining of the molded composites on the basis of the mixtures of the powders of nano-dispersed polyethylene, cellulose and the ultra-dispersed carbonic materials is developed. These materials possess the assigned sorption properties and the physic-mechanical characteristics. They are suitable for the usage at the process of cleaning and separation of gas mixture.

2.1 INTRODUCTION

In solving problems of environmental protection, medicine, cleaning and drying processes of hydrocarbon gases are indispensable effective sorbents, including polymer nanocomposites derived from readily available raw materials.

The nature of the binder and the active components, and molding conditions are especially important at the process of sorption-active composites creating. These factors ultimately exert influence on the development of the porous structure of the sorbent particles and its performance. In this regard, it is promising to use powders of various functional materials having nanoscale particle sizes at the process of such composites creating. First, high degree of homogenization of the components facilitates their treatment process. Secondly, the high dispersibility of the particles allows them to provide a regular distribution in the matrix, whereby it is possible to achieve improved physical and mechanical properties. Third, it is possible to create the composites with necessary sorption, magnetic, dielectric and other special properties combining volumetric content of components [1].

Powders of low density polyethylene (LDPE) prepared by high temperature shearing (HTS) used as one of prospective components of the developing functional composite materials [2, 3].

Development of the preparation process and study of physicochemical and mechanical properties of sorbents based on powder mixtures of LDPE, cellulose (CS) and carbon materials are conducted. As the basic sorbent material new – ultrafine nanocarbon (NC) obtained by the oxidative condensation of methane at a treatment time of 50 min (NC1) and 40 min (NC2) having a specific surface area of 200 m²/g and a particle size of 30–50 nm is selected [4]. Ultrafine form of NC may give rise to technological difficulties, for example, during regeneration of NC after using in gaseous environments, as well as during effective separation of the filtrate from the carbon dust particles. This imposes restrictions on the using of NC as an independent sorbent. In this connection, it should be included in a material that has a high porosity. LDPE and CS powders have great interest for the production of such material. It is known that a mixture of LDPE and CS powders have certain absorption properties, particularly, they were tested as sorbents for purification of water surface from petroleum and other hydrocarbons [5].

Thus, the choice of developing sorbents components is explained by the following reasons:

1. LDPE has a low softening point, allowing to conduct blanks molding at low temperatures. The very small size of the LDPE particles (60 to 150 nm) ensures regular distribution of the binder in the matrix. It is also important that the presence of binder in the composition is necessary for maintaining of the material's shape, size, and mechanical strength.
2. Usage of cellulose in the composite material is determined by features of its chemical structure and properties. CS has developed capillary-porous structure, that's why it has well-known sorption properties [5] towards polar liquids, gases and vapors.
3. Ultrafine carbon components [nanocarbon, activated carbon (AC)] are used as functionalizing addends due to their high specific surface area.

2.2 EXPERIMENTAL PART

Ultrafine powders of LDPE, CS and a mixture of LDPE/CS are obtained by high temperature shearing under simultaneous impact of high pressure and shear deformation in an extrusion type apparatus with a screw diameter of 32 mm [3].

Initial press-powders obtained by two ways. The first method is based on the mechanical mixing of ready LDPE, CS and carbon materials' powders. The second method is based on a preliminary high-shear joint grinding of LDPE pellets and sawdust in a specific ratio and mixing the resulting powder with the powdered activated carbon (BAY-A mark) and the nanocarbon after it.

Composites molding held by thermobaric compression at the pressure of 127 kPa. Measuring of the tablets strength was carried out on the automatic catalysts strength measurer ПК-1.

The adsorption capacity (A) of the samples under static conditions for condensed water vapor, benzene, n-heptane determined by method of complete saturation of the sorbent by adsorbate vapor in standard conditions at 20°C [6] and calculated by the formula: $A = m/(M \cdot d)$, where m is the mass of the adsorbed benzene (acetone, n-heptane), g; M is the mass of the dried sample, g; d is the density of the adsorbate, g/cm³.

Water absorption coefficient of polymeric carbon sorbents is defined by the formula: $K = \frac{m_{\text{absorbed water}}}{m_{\text{sample}}} \times 100\%$, where $m_{\text{absorbed water}}$ is the mass of the water, retained by the sorbent sample, m_{sample} is the mass of the sample.

Experimental error does not exceed 5% in all weight methods at P = 0.95 and the number of repeated experiments n = 3.

2.3 RESULTS AND DISCUSSION

Powder components are used as raw materials for functional composite molding (including the binder LDPE), because molding of melt polymer mixtures with the active components has significant disadvantages. For example, the melt at high degrees of filling loses its fluidity, at low degrees of filling flow rate is maintained, but it is impossible to achieve the required material functionalization.

It is known that amorphous-crystalline polymers, which are typical heterogeneous systems, well exposed to high-temperature shear grinding process. For example, the process of HTS of LDPE almost always achieves a significant results [3]. Disperse composition is the most important feature of powders, obtained as result of high-temperature shear milling. Previously, on the basis of the conventional microscopic measurement, it was believed that sizes of LDPE powder particles obtained by HTS are within 6–30 micrometers. Electron microscopy gives the sizes of 60 to 150 nm. The active powder has a fairly high specific surface area (up to 2.2 m²/g).

The results of measurement of the water absorption coefficient and of the static capacitance of LDPE powder by n-heptane vapor are equal to 12% and 0.26 cm³/g, respectively. Therefore, the surface properties of LDPE powder more developed than the other polyethylene materials'.

Selection of molding conditions of sorbents based on mixtures of LDPE, CS and ultrafine carbon materials' powders.

Initial press-powders are obtained by two ways. The first method is based on the mechanical mixing of ready LDPE, CS and carbon materials' powders and the second method is based on a preliminary high-shear joint grinding of LDPE pellets and sawdust in a specific ratio and mixing the resulting powder with the powdered activated carbon and the nanocarbon after it. The method of molding – thermobaric pressing at a pressure of 127 kPa.

The mixture of LDPE/CS compacted into cylindrical pellets at a temperature of 115–145°C was used as a model mixture for selection of composites molding conditions. Pressing temperature should be such that the LDPE softens but not melts, and at the same time forms a matrix to prevent loss of specific surface area in the ready molded sorbent due to fusion of pores with the binder. The composites molded at a higher temperature, have a lower coefficient of water absorption than the tablets produced at a lower temperature, that's why the lowest pressing temperature (120°C) is selected. At a higher content of LDPE the water absorption coefficient markedly decreases with temperature.

Cellulose has a high degree of swelling in water (450%) [5], this may lead to the destruction of the pellets. Its contents in samples of composites, as it has been observed by the sorption of water, should not exceed 30 wt.%. There is a slight change of geometric dimensions of the pellets in aqueous medium at an optimal value of the water absorption coefficient when the LDPE content is 20 wt.%.

Samples of LDPE/CS with AC, which sorption properties are well studied, are tested for selecting of optimal content of ultrafine carbon. The samples containing

more than 50 wt.% of AC have less water absorption coefficient values. Therefore, the total content of ultrafine carbon materials in all samples must be equal to 50 wt.%.

Static capacitance measurement of samples, obtained from mechanical mixtures of powders of PE, CS and AC, conducted on vapors of n-heptane and benzene, to determine the effect of the polymer matrix on the sorption properties of functionalizing additives. With a decrease of the content of AC in the samples with a fixed (20 wt.%) amount of the binder, reduction of vapor sorption occurs. It indicates that the AC does not lose its adsorption activity in the composition of investigated sorbents.

Strength of samples of sorbents (Fig. 2.1) is in the range of 620–750 N. The value of strength is achieved in the following molding conditions: $t = 120^{\circ}\text{C}$ and a pressure of 127 kPa.

Thus, optimal weight composition of the matrix of LDPE/CS composition – 20/30 wt.% with 50 wt.% containing of carbon materials.

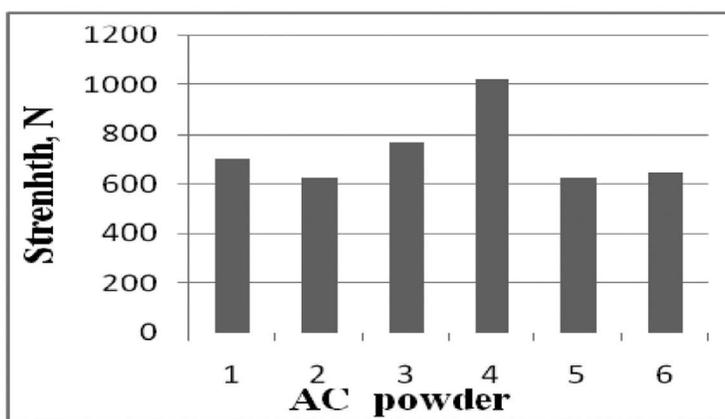


FIGURE 2.1 Comparison of strength of pellets, based on LDPE, CS (different species of wood) and AC powders [1 – sorbent of LDPE/AC/CS = 20/50/30 wt.% based on the powders of jointly dispersed pellets of LDPE and softwood sawdust with subsequently addition of AC; 2 – sorbent of LDPE/AC/CS = 20/50/30 wt.% based on the powders of jointly dispersed pellets of LDPE and hardwood sawdust with subsequently addition of AC; 3 – sorbent of LDPE/AC/CS = 20/50/30 wt.% based on the mechanical mixtures of the individual powders of LDPE, CS from softwood and AC; 4 – AC tablet; 5 – sorbent of LDPE/CS = 20/80 wt.%; 6 – sorbent of LDPE/AC = 20/80 wt.%].

Sorption properties of carbon – polymer composites by condensed vapors of volatile liquids

For a number of samples of sorbents static capacitance values by benzene vapor is identified (Fig. 2.2). They indicate that the molded mechanical mixture of 20/25/25/30 wt.% LDPE/AC/NC1/CS has a maximum adsorption capacity that

greatly exceeds the capacity of activated carbon. High sorption capacity values by benzene vapor appears to be determined by weak specific interaction of π -electron system of the aromatic ring with carbocyclic carbon skeleton of the nanocarbon [7].

Static capacitance of obtained sorbents by heptane vapors significantly inferior to capacity of activated carbon (Fig. 2.3), probably it is determined by the low polarizability of the molecules of low-molecular alkanes. Consequently, the investigated composites selectively absorb benzene and can be used for separation and purification of mixtures of hydrocarbons.

Molded composite based on a mechanical mixture of LDPE/AC/NC1/CS = 20/25/25/30 wt.% has a sorption capacity by acetone vapor comparable with the capacity of activated carbon ($0.36 \text{ cm}^3/\text{g}$) (Fig. 2.4).

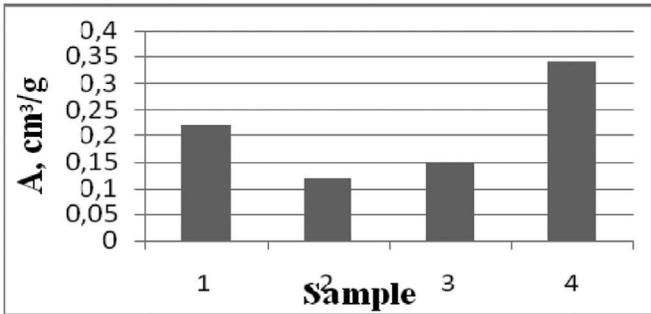


FIGURE 2.2 Static capacitance of sorbents, A (cm^3/g) by benzene vapor (20°C) [1 – molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30wt.%; 2 – molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt.%; 3 – molded mechanical mixture of LDPE/AC/CS=20/50/30 wt.%; 4 – AC medical tablet (controlling)].

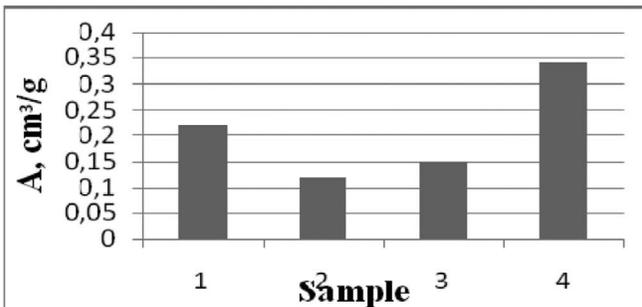


FIGURE 2.3 Static capacitance of sorbents, A (cm^3/g) by n-heptane vapor (20°C). 1 – molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30wt.%; 2 – molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt.%; 3 – molded mechanical mixture of PE/AC/CS=20/50/30 wt.%; 4 – AC medical tablet (controlling).

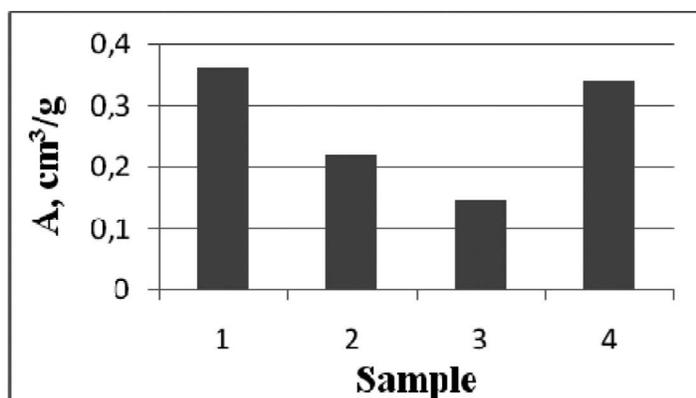


FIGURE 2.4 Static capacitance of sorbents, A (cm³/g) acetone vapor (20°C). 1 – molded mechanical mixture of LDPE/AC/NC1/CS= 20/25/25/30wt.%; 2 – molded mechanical mixture of LDPE/AC/NC2/CS = 20/25/25/30 wt.%; 3 – molded mechanical mixture of LDPE/AC/CS=20/50/30 wt.%; 4 – AC medical tablet (controlling).

Sorbents' samples containing NC2 have low values of static capacity by benzene, heptanes and acetone vapor. It can be probably associated with partial occlusion of carbon material pores by remnants of resinous substances – by products of oxidative condensation of methane, and insufficiently formed porous structure.

The residual benzene content measuring data (Table 2.1) shows that the minimal residual benzene content after its desorption from the pores at $t = 70^{\circ}\text{C}$ for 120 min observes in case of sorbent LDPE/AC/NC1/CS composition = 20/25/25/30 wt.%. It allows to conclude that developed sorbents have better ability to regenerate under these conditions in comparison with activated carbon.

TABLE 2.1 Sorbents' Characteristics: Total Pore Volume V_{tot} ; Static Capacitance (A) by Benzene Vapors at the Sorption Time of 2 days; Residual Weight of the Absorbed Benzene After Drying at $t = 70^{\circ}\text{C}$ for 120 min

LDPE/AC/NC/CS sorbent composition, wt.%	V_{tot} , cm ³ /g	A, cm ³ /g	Residual benzene content as a result of desorption, %
20/25/25/30	1.54	0.5914	2.9
20/50/–/30	1.21	0.1921	10.3
–/100/–/–	1.60	0.3523	32.0

2.4 CONCLUSIONS

Thus, the usage of nanosized LDPE as a binder gives a possibility to get the molded composite materials with acceptable absorption properties. Optimal conditions for molding of sorbents on the basis of mixtures of powdered LDPE, cellulose and ultrafine carbon materials were determined: temperature 120°C and pressure of 127 kPa, content of the binder (polyethylene) is 20 wt.%.

Varying the ratio of the components of the compositions on the basis of ternary and quaternary mixtures of powdered LDPE, cellulose and ultrafine carbon materials it is possible to achieve the selectivity of sorption properties by vapors of certain volatile liquids. Established that molded mechanical mixture of LDPE/AC/NC1/CS 20/25/25/30wt.% has a static capacity by condensed vapors of benzene and acetone 0.6 cm³/g and 0.36 cm³/g, respectively, what exceeds the capacity of activated carbon. The static capacitance of the compositions by the n-heptane vapors is 0.21 cm³/g, therefore, the proposed composites are useful for separation and purification of gaseous and steam mixtures of different nature.

Developed production method of molded sorption-active composites based on ternary and quaternary mixtures of powdered LDPE, cellulose and ultrafine carbon materials can be easily designed by equipment and can be used for industrial production without significant changes.

KEYWORDS

- cellulose
- high-temperature shift crushing
- nano-carbon
- polyethylene
- sorbents

REFERENCES

1. Akbasheva, E. F., & Bazunova, M. V. (2010). Tableted sorbents based on cellulose powder mixtures, polyethylene and ultra-dispersed carbon. Materials Open School Conference of the CIS "Ultrafine and Nanostructured Materials" (11–15 October 2010), Ufa: Bashkir State University, 106.
2. Enikolopyan, N. S., Fridman, M. L., & Karmilov, A. Yu. (1987). Elastic Deformation Grinding of Thermo Plastic Polymers, Reports as USSR, 296(1), 134–138.
3. Akhmetkhanov, R. M., Minsker, K. S., & Zaikov, G. E. (2006). On the Mechanism of Fine Dispersion of Polymer Products at Elastic Deformation Effects. *Plasticheskie Massi*, (8), 6–9.