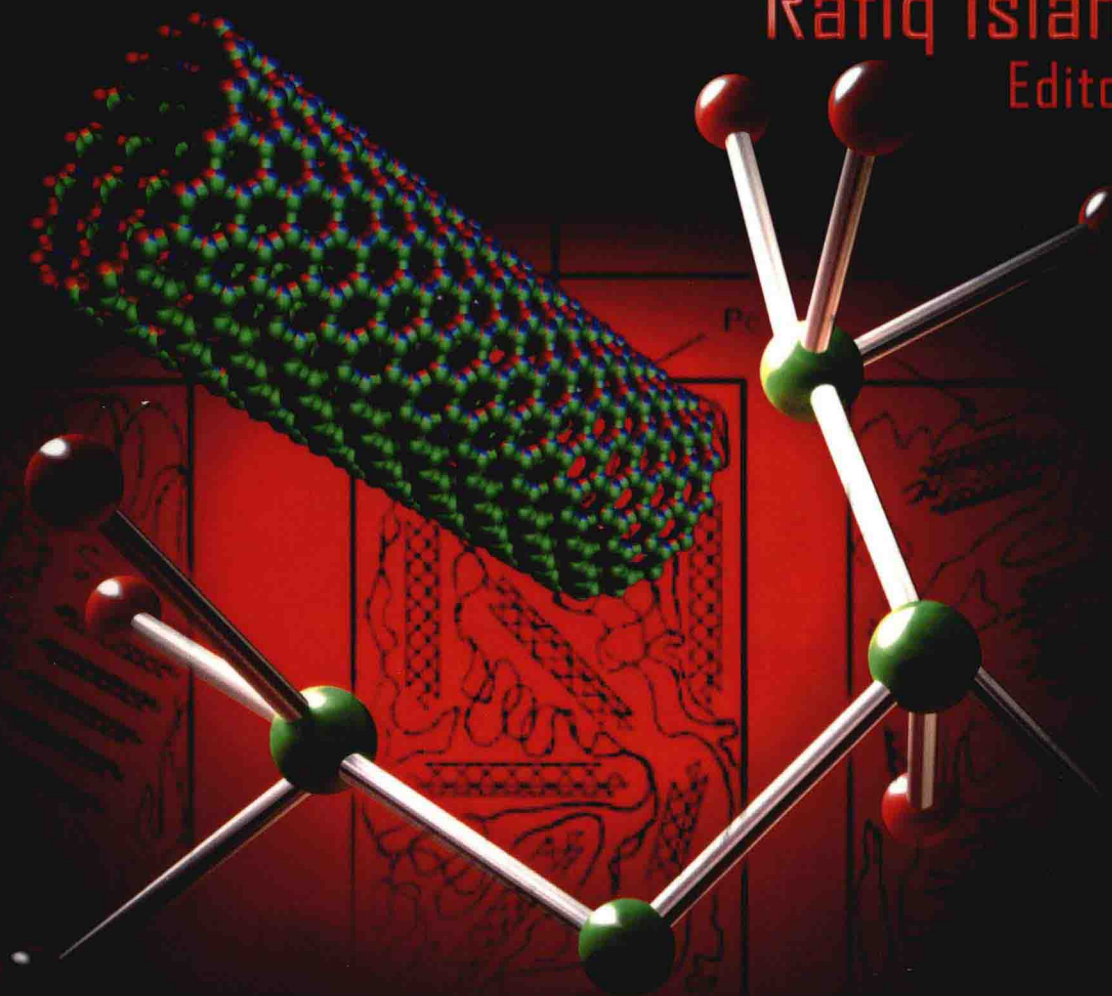


MATERIALS SCIENCE AND TECHNOLOGIES

Characterization and Development of Novel Materials Research Compendium

Rafiq Islam
Editor



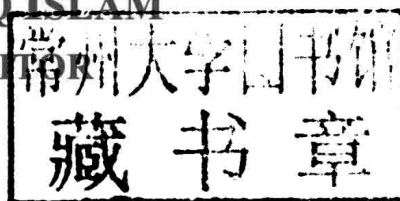
NOVA

MATERIALS SCIENCE AND TECHNOLOGIES

**CHARACTERIZATION
AND DEVELOPMENT OF NOVEL
MATERIALS RESEARCH
COMPENDIUM**

RAFIQ ISLAM

EDITOR



 **nova**
publishers
New York

Copyright © 2013 by Nova Science Publishers, Inc.

All rights reserved. No part of this book may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic, tape, mechanical photocopying, recording or otherwise without the written permission of the Publisher.

For permission to use material from this book please contact us:

Telephone 631-231-7269; Fax 631-231-8175

Web Site: <http://www.novapublishers.com>

NOTICE TO THE READER

The Publisher has taken reasonable care in the preparation of this book, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained in this book. The Publisher shall not be liable for any special, consequential, or exemplary damages resulting, in whole or in part, from the readers' use of, or reliance upon, this material. Any parts of this book based on government reports are so indicated and copyright is claimed for those parts to the extent applicable to compilations of such works.

Independent verification should be sought for any data, advice or recommendations contained in this book. In addition, no responsibility is assumed by the publisher for any injury and/or damage to persons or property arising from any methods, products, instructions, ideas or otherwise contained in this publication.

This publication is designed to provide accurate and authoritative information with regard to the subject matter covered herein. It is sold with the clear understanding that the Publisher is not engaged in rendering legal or any other professional services. If legal or any other expert assistance is required, the services of a competent person should be sought. FROM A DECLARATION OF PARTICIPANTS JOINTLY ADOPTED BY A COMMITTEE OF THE AMERICAN BAR ASSOCIATION AND A COMMITTEE OF PUBLISHERS.

Additional color graphics may be available in the e-book version of this book.

Library of Congress Cataloging-in-Publication Data

ISBN: 978-1-62257-334-9

Published by Nova Science Publishers, Inc. + New York

MATERIALS SCIENCE AND TECHNOLOGIES

**CHARACTERIZATION
AND DEVELOPMENT OF NOVEL
MATERIALS RESEARCH
COMPENDIUM**

MATERIALS SCIENCE AND TECHNOLOGIES

Additional books in this series can be found on Nova's website
under the Series tab.

Additional e-books in this series can be found on Nova's website
under the e-books tab.

NANOTECHNOLOGY SCIENCE AND TECHNOLOGY

Additional books in this series can be found on Nova's website
under the Series tab.

Additional e-books in this series can be found on Nova's website
under the e-books tab.

PREFACE

This book compiles articles from the Journal of Characterization and Development of Novel Materials. Topics discussed include the perspectives of polymer nanocomposites applications as engineering materials; polymeric nanocomposites based on the organomodified layered silicates; structural analysis of nanocomposites polymer/organoclay microhardness and kinetics and mechanism of emulsion copolymerization of methyl acrylate with hydrophilic monomers.

Chapter 1 – It has been shown, that nanoparticles surface dimension is defined by polymer macromolecules ability to “reproduce” its relief. A nanofiller network dimension depends on its anisotropy degree. The indicated dimension value defines modification of matrix polymer structure at nanofiller introduction or its absence. Particulate nanofiller is the most effective one for engineering polymer nanocomposites creation.

Chapter 2 - The analytic review of recent advances in the field of synthesis and study of the structures and properties of the polymeric nanocomposites on the basis of the organomodified layered silicates is given.

Chapter 3 - The analysis of microhardness and yield stress interconnection for nanocomposites polymer/organoclay was carried out within the frameworks of the fractal model. It has been shown, that microhardness and yield stress ratio for such nanocomposites is defined by their structural state only. The indicated state is characterized unequivocally by structure fractal dimension.

Chapter 4 - Emulsion copolymerization of methyl acrylate with metacrylic acid or acrylonitrile was investigated by means of dilatometry and the turbidity spectrum method (measuring the polymerization rate and the number of polymer-monomer particles in the dispersion at several initial conditions and conversion degrees). The discrepancy between the kinetics and mechanism of this process and the classical knowledge of this reaction is due to realization of several nucleation mechanisms; radical–radical interaction in the aqueous phase leading to the formation of surfactant oligomers (which act as an emulsifier) as well as to chain termination; the presence of several growing radicals in polymer-monomer particles and the gel effect manifestation; flocculation of particles at various stages of polymerization; partial dissolution of some of the examined emulsifiers in the monomer. The dependence of the said processes on the comonomer's nature is shown.

Chapter 5 - Contributors gave different examples about using of degradation as a method of modification of polymeric materials for receiving new materials with improved properties. The hydrolysis, ozonolysis and oxidation are acceptable for modification of films, fibres,

membranes and another polymeric materials. Authors recommended new methods of increasing of adhesion of films and fibres.

Chapter 6 - This analytical review presents technological features of "Oyster mushroom mycelium extract 'Ovodorin[®]'" BAA (biologically active additive or dietary supplement) production, characterizes its composition, describes the scope of research and analyzes medical-biological investigation and therapeutic monitoring results of "Oyster mushroom mycelium extract 'Ovodorin[®]'" BAA application as a maintenance agent for cancer patients to eliminate side reactions of chemo- and radiotherapy used that has significantly increased the quality of the complex drug therapy. The area of "Oyster mushroom mycelium extract 'Ovodorin[®]'" BAA is recommended and basic directions for drug creation are specified. The publication is intended for oncologists, radiologists and physicians of other specialties who take up the problem of tumor treatment.

Chapter 7 - New condensation monomers - primarily dinitrocompounds and diamines containing aromatic and aliphatic bulky substituents - were obtained from 2,4,6-trinitrotoluene (TNT) derivatives. Interaction of some dinitrocompounds containing strong electron-withdrawing groups in meta-positions with bis-phenols under conditions of aromatic nucleophilic polynitrosubstitution reactions led to the formation of aromatic oligoethers. On the basis of aromatic diamines containing different substituents under conditions of traditional polycondensation and polycyclocondensation reactions there were obtained aromatic polyamides and polyimides demonstrating improved processability combined with high thermal stability.

Chapter 8 - This paper presents a brief review on three avenues of the formation of nanoparticle/copolymer composites: (i) when nanoparticles (NPs) grow in well-defined cores of block copolymer micelles, (ii) when block copolymer micelles are formed due to metallation, and (iii) when alternating copolymers are used for post-synthesis modification of the nanoparticle surface due to hydrophobic interactions.

Chapter 9 - New magnetic nanomaterials have been synthesized from ferrocene-containing polyphenylenes. Cyclotrimerization of 1,1'-diacetylferrocene by condensation reaction catalyzed by p-toluenesulfonic acid in the presence of triethyl orthoformate both in solution and supercritical carbon dioxide in the temperature range of 70 – 200 °C is described. Highly branched ferrocene-containing polyphenylenes prepared by this procedure were used as precursors for preparing magnetic nanomaterials. This was achieved by thermal treatment of polyphenylenes in the range of 200 – 750 °C. The emerging of crystal magnetite nanoparticles of magnetite with the average size of 6 to 22 nm distributed in polyconjugated carbonized matrix was observed due to crosslinking and thermal degradation of polyphenylene prepolymers. Saturation magnetization of such materials came up to 32 Gs·cm³/g in a field of 2.5 kOe.

Chapter 10 - Photochromism does not have a rigorous definition, but is usually used to describe compounds that undergo a reversible photochemical reaction where an absorption band in the visible part of the electromagnetic spectrum changes dramatically in strength or wavelength. In many cases, an absorbance band is present in only one form. The degree of change required for a photochemical reaction to be dubbed "photochromic" is that which appears dramatic by eye, but in essence there is no dividing line between photochromic reactions and other photochemistry. Some of the most common processes involved in photochromism are pericyclic reactions, cis-trans isomerizations, intramolecular hydrogen transfer, intramolecular group transfers, dissociation processes and electron transfers.

Chapter 11 - The novel polynaphthylimides on the basis of aroilen-bis-(naphthalic anhydrides) and non-traditional aromatic diamines, particularly 3,3'-diamino-4,4'-dichlorarilenes containing chlorine atoms in the bulk, have been obtained. All of them reveal the solubility in dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone and mix phenol to trichlorethane (1 to 3). The values T_g of the polymers vary in range 210-270°C, the temperature of the 10% loss in weight ranges as 480-530°C, flame-resistance (oxygen index) reaches 62,5.

Chapter 12 - For the first time there is formulated a notion of gradiently oriented state. Some regularity for formation of gradiently oriented state in polymers are established. The specificity of influence of non-homogeneous mechanical field has been demonstrated on the example of creation of GB-elements, which is the object of research of the new non-traditional direction of the gradient optics – GB-optics (Gradient Birefringence Optics). Possible spheres of use of GB-elements are polarized compensators, polarized holography and photonics, the interference polarized GB-monochromator, the luminescence analysis, etc.

Chapter 13 - The radical bulk homopolymerization of methyl methacrylate and styrene initiated by benzoyl peroxide or azo-bis-isobutironitrile in the presence of heterocyclic derivatives of ferrocene is studied. It is shown that, in the case of the peroxide initiator, ferrocene derivatives form highly efficient initiation systems, which make it possible to polymerize methyl methacrylate at a high rate, to reduce the molecular mass of polymers, and to synthesize polymers with a high content of syndiotactic triads, while in the case of azo-bis-isobutironitrile, such systems are not formed.

Aim: The purpose of this study is to investigate the radical polymerization of methyl methacrylate and styrene initiated by benzoyl peroxide or azo-bis-isobutironitrile in the presence of heterocyclic derivatives of ferrocene.

Chapter 14 - Studies of thermal and fire-resistant properties of the polypropylene/multi-walled carbon nanotube composites (PP/MWCNT) prepared by means of melt intercalation are discussed. The sets of the data acquired with the aid of non-isothermal TG experiments have been treated by the model kinetic analysis. The thermal-oxidative degradation behavior of PP/MWCNT and stabilizing effect caused by addition of MWCNT has been investigated by means of TGA and EPR spectroscopy. The results of cone calorimetric tests lead to the conclusion that char formation plays a key role in the mechanism of flame retardation for nanocomposites. This could be explained by the specific antioxidant properties and high thermal conductivity of MWCNT which determine high-performance carbonization during thermal degradation process. Comparative analysis of the flammability characteristics for PP-clay/MWCNT nanocomposites was provided in order to emphasize the specific behavior of the nanocomposites under high-temperature tests.

Chapter 15 - By means of the UV, IR, and NMR spectroscopy, densimetry and viscometry reaction of arabinogalactan from Siberian larch with kanamycin in water solutions was studied. The composition and the stability constant of the complex formed were evaluated, and optimal conditions of its synthesis were established. *The aim* of this work is the investigation of the reaction of arabinogalactan with kanamycin by means of spectrophotometry, viscometry, and densimetry, and synthesis of new compounds exhibiting physiological activity.

Chapter 16 - Reaction of low temperature oxidations of ethylene glycol (EG) by molecular oxygen in the presence of salts of bivalent copper and alkali both in water and in waterless solutions was investigated. It was found that at low (close to room) temperatures

and the process carrying out in waterless solutions the basic product of EG oxidation is formic acid. Rise the temperature from 290 – 315 K to 350 – 360 K or carrying out the reaction in the water-containing solutions leads to sharp change of a direction of reaction. EG in these conditions is oxidized with primary formation of glycolic acids salts. Change of a direction of reaction is connected, apparently, with decrease stability of chelate complexes of Cu^{2+} -ions with dianionic form of EG. The mechanism of glycolic acids formation includes, possibly, a stage of two-electronic reduction of O_2 in reaction of dioxygen with monoanionic forms of EG, coordinated on Cu^{2+} -centers.

Chapter 17 - Influence of turbulent hashing on laws of butadiene polymerization at presence $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ is investigated. At turbulent hashing at the initial moment of polymerization there is an increase of polymerization speed due to growth of concentration of the active centers. Whereas at hashing at the certain conversion a monomer the speed increase is observed due to increase of constant of rate reaction of growth polymeric chain. In all cases polybutadiene is characterized by narrower MWD. Thus it is established that the diffusion resistance are not the determining factor in the polymerization of butadiene to a certain level of conversion.

Chapter 18 - Adhesion interaction of the most widely distributed species of microscopic fungi: *Aspergillus niger*, *Trichoderma viride*, *Penicillium funiculosum*, *Aspergillus terreus* to surfaces of materials (polymers, metals) is studied. The force of adhesion interaction was measured by the method of centrifugal detachment. On the base of analysis of kinetic curves the macroscopic characteristics of adhesion micro-organism–metal surface were obtained. Author show on the example of *Aspergillus niger* that stochastic nature of adhesion of microorganisms cells is caused by heterogeneity of support surface, heterogeneity of conidium sizes, and distribution of them by forces of adhesion obeys the Gauss law. Author established that structure of cellular wall of microscopic fungi was changed in dependence on age, and change of force of adhesion interaction correlated with changes in cellular wall structure of microscopic fungi, and dominating role in strengthening of adhesion interaction was played by increase of albuminous components concentration in surface layer of cell.

Chapter 19 - A reactivity of *N*-allylated monomers of new structural types – *N,N*-diallyl-*N'*-acylhydrazines, 2,2-diallyl-1,1,3,3-tetraethylguanidinium-chloride, tris(diethylamino) diallylaminophosphonium tetrafluoroborate and chloride in reactions of free-radical homo- and copolymerization with sulphur dioxide has been studied. The structure of the obtained polysulphones has been identified by ^{13}C NMR. The carried out investigations have shown that these new allyl monomers copolymerize with SO_2 both double bonds participating with formation of cis-, trans-stereoisomeric pyrrolidine structures in a cyclolinear polymer chain. The cyclolinear copolymers obtained are soluble due to the intramolecular cyclization of allyl monomers during the formation of the polymer chain and to the absence of intermolecular crosslinks.

Chapter 20 - The synthesis of new α -amino acid based bioanalogous (ABBA) polymers with non-natural architecture of macromolecules is overviewed. This new architecture implies the orientation of amino acids in the polymeric backbones that differs from their directional head-to-tail orientation in naturally occurring polymers like polypeptides and proteins along with chemical linkages other than amide (peptide) bonds. It is expected that this new macromolecular architecture imparts at least low immunogenicity to the polymers composed of physiological building blocks – α -amino acids. Various polyfunctional amino acids like

diamino- α -carboxylic acids, α -amino-dicarboxylic acids, and tyrosine as well as dimerized α -amino acid like N,N'-diacyl-*bis*- α -amino acids and bis-(α -amino acid)-alkylene diesters were used as key building blocks for designing the ABBA polymers. The ABBA polymers were synthesized by various polycondensation methods under mild conditions without using any toxic catalyst or reagent. The obtained polymers have material properties apt for their applications as surgical implants and drug eluting / delivering devices.

Chapter 21 - Nonuniformity of active sites in stereoregulation ability and kinetic activity of titanium-containing catalytic system has been investigated. It has been shown that in the studied range of ratios of Al/Ti at maximum six types of active sites different in stereoregulation ability and four ones different in their kinetic activity can be formed. A correlation between the effects of kinetic activity and stereospecificity of separate types of active sites has been found. Kinetic parameters for individual types of active sites have been obtained by solving reverse kinetics tasks.

Chapter 22 - The influence of strain in the reaction center containing a double bond on double bond reactivity at the first stage of the reaction with ozone was studied by the B3LYP density functional theory method and ab initio MP2, CCSD, QCISD, and MRMP2 multireference methods. The 6-31+G** and 6-311+G** basis sets were used. The reactions of ozone with ethylene and butylene were studied. Deformation (ϵ) was introduced by using the C=C bond length or the distance between extreme carbon atoms as a coordinate not subjected to optimization. Stretching of the double bond was found to activate the reaction by the mechanisms of symmetrical and nonsymmetrical addition. The sensitivities to deformation were similar in the two channels. When the butene fragment as a whole was stretched, a different picture was observed, and the reaction with ozone was decelerated. In both cases, the logarithms of rate constants linearly depended on ϵ . The calculation results were analyzed using the approach developed earlier, which allowed the calculation results to be used to obtain an analytic form of the dependence of activation energy E_a on the strength of bonds and to relate deformation-induced changes in E_a to the length and rigidity of the initial and transition states.

Chapter 23 - On the base of quantum chemical calculations the most probable reactions between zirconocene dichloride, methyl methacrylate and poly(methyl methacrylate) growing radical were revealed. The reasons of regulating effect of zirconocene dichloride upon free radical polymerization of MMA were analyzed.

Chapter 24 - The UQCISD, UB3LYP, UMP2, and MRMP2 methods in conjunction with the 6-31+G**/6-311+G** and aug-cc-PVDZ basis sets are used to study the primary reaction of ozone with chlorinated ethylene derivatives: tetrachloroethylene, trichloroethylene, 1,2-*trans*-dichloroethylene, 1,2-*cis*-dichloroethylene, 1,1-dichloroethylene, and chloroethylene. The reaction is studied for both concerted and nonconcerted ozone addition. The UB3LYP DFT method in conjunction with the 6-31+G** basis set is used to examine various modes of addition of ozone to these chlorinated ethylenes by the Criegee and DeMore mechanisms. The geometry and energy of the transition states, the enthalpy and entropy, and the rate constants and ratios thereof for all the reactions are calculated. The UB3LYP method generally satisfactorily describes the two reaction pathways and, largely correctly predicts the rate constants, in agreement with the available experimental data. At the same time, this method appears to be inapplicable to modeling the interaction of ozone with 1,1-dichloroethylene. In this case, the single determinant approximation turns out to be

unsuitable, and, therefore, MCSCF methods should be used. The MRMP2 method yields reasonable values of the rate constants for the DeMore mechanism, whereas in the case of the Criegee mechanism, the MP2 method does well. The UB3LYP/6-31+G** and UQCISD/aug-cc-PVDZ methods give similar values of the ratio between the rate constants for the two pathways, a result that demonstrates the versatility of the first one.

Versions of these chapters were also published in *Journal of Characterization and Development of Novel Materials*, Volume 2, Numbers 1-4, published by Nova Science Publishers, Inc. They were submitted for appropriate modifications in an effort to encourage wider dissemination of research.

CONTENTS

Preface		ix
Chapter 1	The Perspectives of Polymer Nanocomposites Applications as Engineering Materials <i>G. V. Kozlov and G. E. Zaikov</i>	1
Chapter 2	Polymeric Nanocomposites Based on the Organomodified Layered Silicates: Structure, Manufacture and Properties <i>A. K. Mikitaev, A. Yu. Bedanokov and M. A. Mikitaev</i>	9
Chapter 3	Structural Analysis of Nanocomposites Polymer/Organoclay Microhardness <i>B. Zh. Dzhangurazov, G. V. Kozlov, G. E. Zaikov, and A. K. Mikitaev</i>	33
Chapter 4	Kinetics and Mechanism of Emulsion Copolymerization of Methyl Acrylate with Hydrophilic Monomers <i>N. V. Kozhevnikov, M. D. Goldfein and N. I. Kozhevnikova</i>	39
Chapter 5	Degradation as a Method of Properties Improving for Polymer Materials <i>S. D. Razumovskii and G. E. Zaikov</i>	47
Chapter 6	Application of a New Polyfunctional Preparation "Oyster Mushroom Mycelium Extract 'Ovodorin [®] '" to the Correction of Drug Intolerance in the Complex Treatment of Oncological Diseases: The Overview of Cytological, Biological and Medical Results <i>V. P. Gerasimenia, S. V. Zakharov, V. Yu. Polyakov, G. I. Kirianov, K. Z. Gumargalieva, L. A. Putyrskiy, Yu. L. Putyrskiy and T. I. Milevich</i>	71

Chapter 7	New Condensation Monomers and Polymers Based on TNT-Derivatives	107
	<i>A. L. Rusanov, L. G. Komarova, V. A. Tartakovskiy, S. A. Shevelev, M. J. M. Abadie, and V. Yu. Voitekunas</i>	
Chapter 8	Copolymers as Stabilizing Media for Nanoparticles	159
	<i>Lyudmila M. Bronstein</i>	
Chapter 9	Ferrocene-Containing Polyphenylenes as Precursors for Magnetic Nanomaterials	169
	<i>R. A. Dvorikova, Yu. V. Korshak, L. N. Nikitin, M. I. Buzin, V. A. Shanditsev, Z. S. Klemenkova, A. L. Rusanov, A. R. Khokhlov, A. Lappas and A. Kostopoulou</i>	
Chapter 10	Organosilicon Polymers with Photoswitchable Fragments in the Side Chain	183
	<i>M. Doroshenko, K. Koynov, G. Zaikov, and O. Mukbaniania</i>	
Chapter 11	The Novel Polynaphthylimides of Improved Solubility on the Basis of Derivatives from Chloral and Dichlordiphenyltrichlorethane	187
	<i>R. M. Koumykov, A. K. Mikitaev and A. L. Rusanov</i>	
Chapter 12	Gradient-Oriented State of Polymers: Formation and Investigation	193
	<i>Levan Nadareishvili, Zurab Wardosanidze, Nodar Lekishvili, Nona Topuridze, Gennady Zaikov and Ryszard Kozlowski</i>	
Chapter 13	Heterocyclic Derivatives of Ferrocene for Radical Polymerization of Methyl Methacrylate and Styrene	205
	<i>Yu. B. Monakov, R. M. Islamova, O. I. Golovochesova, and O. N. Chupakhin</i>	
Chapter 14	Thermal Degradation and Combustion Behavior of Polypropylene/Multiwalled Carbon Nanotube Composites	221
	<i>G. E. Zaikov and S. M. Lomakin</i>	
Chapter 15	Complex Formation of Arabinogalactan from the Siberian Larch with Kanamycin	237
	<i>Yu. B. Monakov, R. Kh. Mudarisova, L. A. Badykova, and E. I. Koptyaeva</i>	

Chapter 16	Catalytic Oxidation of Ethylene Glycol by Dioxygen in Alkaline Medium: The New Example of One-Stage Oxidative Cleavage of C-C Bond <i>A. M. Sakharov, P. A. Sakharov and G. E. Zaikov</i>	245
Chapter 17	Control Factors of Butadiene Stereospecific Polymerization under the Conditions of Catalyst Kinetic Nonuniformity and Viscosity Increase <i>Yu. B. Monakov, V. P. Zakharov and V. Z. Mingaleev</i>	255
Chapter 18	Adhesion of Microorganisms to Materials' Surfaces <i>Klara Z. Gumargalieva, Irina G. Kalinina, Sergei A. Semenov, Gennady E. Zaikov, Lidiya A. Zimina and Marina I. Artsis</i>	267
Chapter 19	The Structure of Polysulphones Based on New <i>N</i> -Allylated Monomers <i>Yu. B. Monakov, M. N. Gorbunova, A. I. Vorob'eva, R. R. Muslukhov and S. V. Kolesov</i>	283
Chapter 20	Non-Conventional Polymers Composed of Naturally Occurring α -Amino Acids <i>Ramaz Katsarava and David Tugushi</i>	295
Chapter 21	Interaction between Kinetic and Stereoregulating Heterogeneity of Active Sites of Titanium Catalyst System in Butadiene Polymerization <i>Yu. B. Monakov, N. N. Sigaeve and Ye. A. Glukhov</i>	315
Chapter 22	Effect of Deformation on the Reactivity of C=C Bonds in Reactions with Ozone <i>B. E. Krisyuk, A. V. Maiorov, V. A. Ovchinnikov and A. A. Popov</i>	335
Chapter 23	DFT Study of Free Radical Polymerization of Methyl Methacrylate in the Presence of Zirconocene Dichloride <i>A. K. Friesen</i>	347
Chapter 24	The Influence of Chlorine Atoms in Chlorinated Ethylene on the Mechanism and Rate of Its Reaction with Ozone <i>B. E. Krisyuk, A. V. Maiorov, E. A. Mamin and A. A. Popov</i>	357
Index		371

Chapter 1

THE PERSPECTIVES OF POLYMER NANOCOMPOSITES APPLICATIONS AS ENGINEERING MATERIALS

G. V. Kozlov^{1*} and G. E. Zaikov^{2#}

¹Kabardino-Balkarian State University,
Nal'chik, Russia

²N.M. Emanuel Institute of Biochemical Physics
of Russian Academy of Sciences,
Moscow, Russia

ABSTRACT

It has been shown, that nanoparticles surface dimension is defined by polymer macromolecules ability to “reproduce” its relief. A nanofiller network dimension depends on its anisotropy degree. The indicated dimension value defines modification of matrix polymer structure at nanofiller introduction or its absence. Particulate nanofiller is the most effective one for engineering polymer nanocomposites creation.

Keywords: Nanocomposites, structure, nanotechnology, organoclay, mechanical properties

INTRODUCTION

As present three main types of nanofillers for polymers can be distinguished: ultrafine particulates, organoclay and carbon nanotubes. A large enough number of nanotubes was obtained on the bases of all sorts of polymers with indicated nanofillers using [1].

But some more optimistic expectations are available about possibilities of high-modulus polymer nanocomposites receiving, particularly in case of carbon nanotubes (CNT) application. These expectations are based on very high CNT modulus (up to 200 GPa [2]) and

* G. V. Kozlov. Kabardino-Balkarian State University, Nal'chik-360004, Russian Federation.

Corresponding author: G. E. Zaikov. N.M. Emanuel Institute of Biochemical Physics of Russian Academy of Sciences, Moscow-119334, Russian Federation. E-mail: I_dolbin@mail.ru.

nanocomposites theoretical treatment within the frameworks of numerous micromechanical models [3]. The indicated models are included in composites elasticity modulus calculation the corresponding parameter for filler and suppose two mentioned characteristics interconnection. However, the models have appeared lately, which do not account for filler elasticity modulus percolation [4] and fractal [5] ones.

Besides, micromechanical models do not take into consideration such important (and often critical) for polymer composites parameters as interfacial adhesion level and initial filler particles aggregation degree. The purpose of the present paper is theoretical analysis of the indicated above nanofillers application perspectives for engineering polymer nanocomposites creation, in case of which reinforcement degree, i.e. nanocomposite elasticity modulus increasing relatively matrix polymer, is an efficiency main indicator.

THEORETICAL ANALYSIS

Within the frameworks of modified percolation model polymer nanocomposites reinforcement degree E_n/E_m can be described as follows [1]:

$$\frac{E_n}{E_m} = 1 + 11(\varphi_n + \varphi_{if})^{1.7}, \quad (1)$$

where E_n and E_m are elasticity moduli of nanocomposite and matrix polymer, φ_n and φ_{if} are nanofiller and interfacial regions relative volume fractions, accordingly.

Let us note, that correctness of interfacial regions treatment as reinforcing element for nanocomposites was confirmed experimentally with the aid of nanoscopic techniques on the example of particulate-filled nanocomposites butadiene-styrene rubber/nanoshungite: in this case interfacial regions elasticity modulus is only on 20 % lower than corresponding parameter for nanoshungite, but in 6 times higher than polymer matrix elasticity modulus [6]. In such treatment nanofiller particles (particles aggregates) surface structure, characterized by its fractal dimension d_{surf} , acquires a particular significance, which defines actually both interfacial regions relative fraction φ_{if} and reinforcement degree E_n/E_m [1]:

$$\varphi_{if} = 0.61(d_{surf} - 2), \quad (2)$$

$$\frac{E_n}{E_m} = 18 \left[1 - (d - d_{surf})^{1/1.7} \right], \quad (3)$$

where d is the dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case $d=3$).

It is easy to see, that the equations (2) and (3) predict reinforcement degree enhancement at the growth of dimension d_{surf} , which can be determined theoretically as follows. First a nanofiller particles specific surface S_u is determined according to the equation [4]: