# Engineering of Polymers and Chemical Complexity

## Volume 2 New Approaches, Limitations, and Control

Editors
Walter W. Focke, PhD
Hans-Joachim Radusch, PhD

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# ENGINEERING OF POLYMERS AND CHEMICAL COMPLEXITY

## Volume II: New Approaches, Limitations, and Control

*Edited by*

**Walter W. Focke, PhD and Hans-Joachim Radusch, PhD**

**Gennady E. Zaikov, DSc and A. K. Haghi, PhD**

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# ENGINEERING OF POLYMERS AND CHEMICAL COMPLEXITY

Volume II: New Approaches, Limitations, and Control

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| AFD | Average fiber diameter |
| ALS | Amyotrophic lateral sclerosis |
| ANN | Artificial neural network |
| ANOVA | Analysis of variance |
| ARDS | Respiratory distress syndrome |
| CA | Contact angle |
| CCBB | Continuous Configurational Boltzmann Biased |
| CCD | Central composite design |
| CNS | Central nervous system |
| CTMP | Chemithermomechanical pulp |
| CVD | Chemical vapor deposition |
| DB | Degree of branching |
| DCSBD | Diffuse coplanar surface barrier discharge |
| DFT | Density functional theory |
| DFT | Density functional theory |
| FP | Ferrocene-containing polymers |
| HBPs | Hyperbranched polymers |
| HLB | Low hydrophilic/lipophilic balance |
| IBD | Inflammatory bowel disease |
| IMP | Integral membrane protein |
| IRMOFs | Isoreticular metal-organic frameworks |
| LDA | Local density approximation |
| LW/AB | Lifshitz-van der Waals/acid-base |
| MD | Molecular dynamics |
| MOF | Metal-organic frameworks |
| NEMD | Non-equilibrium molecular dynamics |
| NSAIDs | Non-steroidal anti-inflammatory drugs |
| PSM | Post-synthetic modification |
| ROS | Reactive oxygen species |
| RSM | Response surface methodology |
| RWFT | Random walks in fractal time |
| SAIA | Slovak Academic Information Agency |
| SBUs | Secondary building units |
| SEM | Scanning electron microscopy |
| SF | Synovial fluid |
| STM | Scanning tunneling microscope |
| TBMD | Tight bonding molecular dynamics |
| TEM | Transmission electron |

# PREFACE

In studies of polymers and chemical complexity, we have designed a broad spectrum of new polymeric materials with unique architectures significant for emerging technologies. New experimental techniques are presented and sophisticated instrumentation are introduced about phenomena occurring at polymer surfaces and interfaces and how polymers diffuse or fracture. These advances in the understanding of polymer systems and chemical complexity are highlighted in the second volume of this series.

In the first chapter, application of polymeric nanocomposites filled with nanoparticles are introduced in detail. Dendritic architectures, as highly branched and three-dimensional macromolecules that have unique chemical and physical properties, offer potential as the next great technological revolution. Chapter 2 gives a brief introduction to some of the structural properties and application of dendritic polymer in various fields. The focus of this chapter is a survey of multi-scale modeling and simulation techniques in hyperbranched polymer and dendrimers. Results of modeling and simulation calculations on dendritic architecture are also reviewed. Polymer nanocomposites are commonly defined as the combination of a polymer matrix and additives that have at least one dimension in the nanometer range. One of the most important fields which have gained an increasing interest in recent years is magnetic nanocomposites. In chapter 3, the basics of magnetic properties of materials are presented along with emulsion polymerization approach to magnetic latexes. In chapter 4, the fractal analysis of polymerization kinetics in nanofiller presence was performed. The influence of catalyst structural features on chemical reaction course was shown.

One of the current trends in the synthesis of polyimides is the creation of fusible and soluble in organic solvents materials. This allows extending the range of their practical use and refines the classical methods for thermoplastics. This problem is particularly relevant in cases when the traditional scheme of high temperature prepolymer conversion into the final polymer, which usually takes place in the final product, cannot be carried out due to thermal instability of the product elements. It is often achieved by the use of monomers (diamines and dianhydrides) with bulky side groups for the synthesis of polyimides. The synthesis of polymers from a mixture of several diamines and dianhydrides, and especially the synthesis of block copolyimides, represents wide opportunities of directed regulation of polyimides properties, including giving them solubility. One of the methods of the block copolymers synthesis is getting them on the basis of pre-synthesized oligomers with determination molecular weight and with different functional groups.

Therefore in chapter 5, the synthesis of poly (4,4'-dipheniloxide)pyromellit(amic acid) (PAA), fragmented by oligo(amic acid) (OAA), obtained by low-temperature

polycondensation of 4,4'-diaminodiphenyl oxide and dianhydride 4,4′-diphenyl-1,5-diazobicyclo/3,3,0/octane-2,3,6,7-tetracarboxilic acid and its subsequent chemical imidization. In the opposition to the original poly-(4,4'-aminodiphenyl)-pyromellitimide (PI) synthesized block copolyimides (BSPI) have a solubility in polar aprotonic solvents. The parameter of BSPI conformation was calculated to explain its solubility.

Chapter 6 describes oxidation stress -source and effects- Hyaluronan origin, properties and functions, and finally thiol compounds as antioxidants preventing HA degradations under conditions of oxidation stress.

In chapter 7, 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 orthoformiate both in solution and supercritical carbon dioxide in the temperature range of 70–200°C 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 6–22 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 filed of 2.5 kOe.

In chapter 8, synthesis and structural properties of MOFs are summarized and some of the key advances that have been made in the application of these nanoporous materials in textile fibers are highlighted.

In chapter 9, a study has been conducted to investigate the relationship between four electrospinning parameters (solution concentration, applied voltage, tip to collector distance, and volume flow rate) and electrospun PAN nanofiber mat properties such as average fiber diameter (AFD) and contact angle (CA).

In chapter 10, the influence of four electrospinning parameters, comprising solution concentration, applied voltage, tip to collector distance, and volume flow rate on the CA of the electrospun PAN nanofiber mat was carried out using response surface methodology (RSM) and artificial neural network (ANN). First, a central composite design (CCD) was used to evaluate main and combined effects of above parameters. Then, these independent parameters were fed as inputs to an ANN while the output of the network was the CA of electrospun fiber mat. Finally, the importance of each electrospinning parameters on the variation of CA of electrospun fiber mat was determined and comparison of predicted CA value using RSM and ANN are discussed.

In chapter 11, the influence of crystalline morphology on fractal space formation for nanocomposites polymer/organoclay is presented.

In chapter 12, the fractal model of coke residue formation for composites high density polyethylene/aluminum hydroxide is described.

In chapter 13, the structural model of nanocomposites Poly(Vinyl Chloride)/ organoclay flame-resistance is studied.

Calculation of efficiency of sedimentation of dispersion particles in A Rotoklon on the basis of model of hydrodynamic interacting of phases is presented in chapter 14.

In this book, we first briefly review the structure, properties, and application of dendritic macromolecules in various fields. Next, molecular simulation techniques in hyperbranched polymer and dendrimers is reviewed. Lastly, we will survey the most characteristic and important recent examples in molecular simulation of dendritic architectures.

Chapter 15 is about hyaluronan; a harbinger of the status and functionality of the joint, and the chapter 16 studies the polyvinylchloride antibacterial pre-treated by barrier plasma.

This new volume provides a balance between materials science and mechanics aspects, basic and applied research, and high technology composite development.

**— Walter W. Focke, PhD and Hans-Joachim Radusch, PhD**

# CONTENTS

## CHAPTER 1

# POLYMERIC NANOCOMPOSITES: STRUCTURE, MANUFACTURE, AND PROPERTIES

A. K. MIKITAEV, A. YU. BEDANOKOV, and M. A. MIKITAEV

## CONTENTS

## 1.1 INTRODUCTION

The polymeric nanocomposites are the polymers filled with nanoparticles which interact with the polymeric matrix on the molecular level in contrary to the macrointeraction in composite materials. Mentioned nanointeraction results in high adhesion hardness of the polymeric matrix to the nanoparticles [1,52].Usual nanoparticle is less than 100 nanometers in any dimension, 1 nanometer being the billionth part of a meter [1,2].

The analysis of the reported studies tells that the investigations in the field of the polymeric nanocomposite materials are very promising.

The first notion of the polymeric nanocomposites was given in patent in 1950 [3]. Blumstain pointed in 1961 [4] that polymeric clay – based nanocomposites had increased thermal stability. It was demonstrated using the data of the thermogravimetric analysis that the polymethylmetacrylate intercalated into the $Na^+$ - methylmetacrylate possessed the temperature of destruction 40–50°C higher than the initial sample.

This branch of the polymeric chemistry did not attract much attention until 1990 when the group of scientists from the Toyota Concern working on the polyamide – based nanocomposites [5-9] found two – times increase in the elasticity modulus using only 4.7 weight% of the inorganic compound and 100°C increase in the temperature of destruction, both discoveries widely extending the area of application of the polyamide. The polymeric nanocomposites based on the layered silicates began being intensively studied in state, academic and industrial laboratories all over the world only after that.

## 1.2 STRUCTURE OF THE LAYERED SILICATES

The study of the polymeric nanocomposites on the basis of the modified layered silicates (broadly distributed and well—known as various clays) is of much interest. The natural layered inorganic structures used in producing the polymeric nanocomposites are the montmorillonite [10-12], hectorite [13], vermiculite [14], kaolin, saponine [15], and others. The sizes of inorganic layers are about 220 and 1 nanometers in length and width respectively [16,17].

The perspective ones are the bentonite breeds of clays which include at least 70% of the minerals from the montmorillonite group.

Montmorillonite $(Na,K,Ca)(Al,Fe,Mg)[(Si,Al)_4O_{10}](OH)_2 \cdot nH_2O$, named after the province Montmorillion in France, is the high – dispersed layered aluminous silicate of white or gray color in which appears the excess negative charge due to the nonstoichiometric replacements of the cations of the crystal lattice, charge being balanced by the exchange cations from the interlayer space. The main feature of the montmorillonite is its ability to adsorb ions, generally cations, and to exchange them. It produces plastic masses with water and may enlarge itself 10 times. Montmorillonite enters the bentonite clays (the term "bentonite" is given after the place Benton in USA).

The inorganic layers of clays arrange the complexes with the gaps called layers or galleries. The isomorphic replacement within the layers (such as $Mg^{2+}$ replacing $Al^{3+}$ in octahedral structure or $Al^{3+}$ replacing $Si^{4+}$ in tetrahedral one) generates the negative charges which electrostatically are compensated by the cations of the alkali or alkali-