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Advances in Polymer Science

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Manfred Klüppel
Editors

Designing of Elastomer Nanocomposites: From Theory to Applications

With contributions by

D. Basu · R. Behnke · A.K. Bhowmick · J.J.C. Busfield ·
N. Chatti · A. Das · F. Fleck · R. Ghosal · T. Horst ·
I. Ivaneiko · M. Kaliske · C.W. Karl · M. Klüppel · M. Koishi ·
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Dedication

Gert Heinrich (Photo by Kai Uhlig, Dresden)

To sum up Gert Heinrich's scientific lifetime achievement in one word, "networks" would be the most accurate description. The molecular networks he worked on during his career were mostly those in filled elastomers and his studies ranged from their theoretical physical description to the testing of tire materials, so we titled this special issue in honor of Gert Heinrich "*Designing of Elastomer Nanocomposites: From Theory to Applications*."

Gert Heinrich's roots are in the Vogtland, a region reaching across the German free states of Bavaria, Saxony, and Thuringia, where he was born in 1950. Even when busy in other parts of the world, he kept faith with his origins, for example, by holding an annual extended weekend with his PhD students in his home town of Pausa. After finishing school and an apprenticeship as bricklayer, he started studies in physics at the Friedrich Schiller University in Jena and graduated as physicist in theoretical physics (applied quantum physics) in 1973. At the Technical University (TH) Merseburg, Department of Polymer Physics, G. Heinrich gained his doctorate in 1978 on the topic "Mechanical properties of polymer networks and statistical-mechanical approaches." As assistant professor at the TH Merseburg he taught polymer physics, experimental physics, and theoretical physics, qualifying as full professor (*Habilitation* and *facultas docendi*) in 1986 with the post-doctoral dissertation "Theory of polymer networks and topological constraints of network chains." He continued his teaching activities as Associate Professor for Theoretical Physics until 1990. After the political changes in East Germany and German reunification, he was eager to apply his extensive and comprehensive knowledge of polymer physics to more application-oriented tasks and accepted a position at the tire manufacturer Continental AG in Hanover as senior research scientist. In addition to his tasks as Head of Materials Research/Strategic Technology at Continental, G. Heinrich also continued his academic activities as lecturer in "Physics and technology of polymers" at the University of Hanover and "Elastomer materials and testing" at the Martin Luther University Halle/Wittenberg. In 2003, he was appointed as full professor for "Polymer materials science" at the Technical University Dresden and, simultaneously, as head of the Institute of Polymer Materials at the Leibniz Institute of Polymer Research Dresden e. V. (IPF). Gert Heinrich was also offered the Professorship for Micro- and Nanostructure-Based Polymer Composites at the Martin Luther University Halle/Wittenberg and the Fraunhofer Institute for Mechanics of Materials (IWM) in 2009. However, he declined the position because his chair at TU Dresden became more distinguished and was designated "Professorship for Polymer Materials and Rubber Technology." In 2015 he was honored three times, receiving the George Stafford Whitby Award for distinguished teaching and research from the Rubber Division of the American Chemical Society; the Colwyn Medal for outstanding services to the rubber industry from the Institute of Materials, Minerals and Mining (IOM3); and the Carl Dietrich Harries Medal from the Deutsche Kautschuk-Gesellschaft (German Rubber Society).

Gert Heinrich's contribution to elastomer research covers several topics. The most prominent works in polymer physics are probably his contributions on the non-affine tube model of rubber elasticity, developed during his time in Merseburg [1]. A first rigorous statistical-mechanical network theory for filled rubbers was published together with Thomas Vilgis [2]. An extension of the Merseburg model to account for the finite extensibility of network chains was made in his first collaboration with Manfred Klüppel, showing that the non-affine tube deformation is well suited for describing the stress–strain response of technical sulfur-cured rubbers [3, 4]. Later, together with Michael Kaliske in Hanover, the non-affine tube model was further extended and implemented into a finite element code [5, 6]. In a comparison of 20 hyperelastic models for rubber-like materials [7] this extended tube model gave the best fit to experimental data and, moreover, involves only four parameters and its derivation is physically motivated. In his work on the physics of tires, Gert Heinrich authored several papers that generated the interest of specialists across the broad field of tire and rubber technology. His high-impact contributions on this topic range from the influence of filler networking on tire performance [2, 8] to the wet skid, wear, and rolling resistance of tire materials [9, 10], to name just a few. Within this framework, a rigorous and fundamental theory of rubber friction on rough surfaces was also developed that accounts for the multiscale excitation of skidding tires on wet tracks [11]. It is less well known that several fundamental results in all these fields were incorporated into R&D projects of Continental AG, recorded in more than 40 internal research reports by G. Heinrich and in several patent applications. In Dresden, intense activity began together with A. Das and K. W. Stöckelhuber on the development and understanding of new elastomeric materials incorporating several species of nanoparticles (layered silicates [12], carbon nanotubes [13], layered double hydroxides [14], haloysite nanotubes [15], graphene nanoplatelets [16]) as fillers. In addition, G. Heinrich delivered significant contributions on the fracture mechanics of elastomers [17] as organizer and spokesperson of research unit FOR 597, Fracture Mechanics and Statistical Mechanics of Reinforced Elastomeric Blends, of the German Research Foundation (DFG). Evaluation of the dynamic properties of rubber composites based on a theoretical, physically motivated multiscale approach [18] is another important point on his scientific agenda. Finally, it should be noted that in Dresden G. Heinrich supervised dozens of graduate students in engineering science and more than 40 PhD students in several branches of polymer materials, polymer processing, and modeling, with topics ranging from elastomers, thermoplastics, thermoplastic elastomers and vulcanizates, and biopolymer materials to composites for lightweight applications.

When Gert Heinrich was awarded the Colwyn Medal, it was stated about his time in Dresden: “He has grown the activity in elastomer research from a relatively modest beginning to be the largest academic group of researchers in Europe. He currently has the greatest publication record of any researcher in the EU with more than 330 journal papers listed on the Web of Science and he has the highest *h*-index of any academic in the EU who works in traditional elastomer/rubber materials.” For the magazine *Tire Technology International*, he was just “Mr. Tire Materials.”

Gert Heinrich has been married to his wife Nelly since 1975 and has two grown-up daughters.

For the up-coming stage of life, we wish him an ideal balance between repose and relaxation in his private life and continuing professional activities as advisor and consultant for science and industry.

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Preface

Rubber plays an important role as a material in modern technologies for mobility, production, and resource extraction. The unique elastic properties of this material facilitate a multitude of technologies to produce items as diverse as car tires, conveyor belts, sealings, bushes, and bearings. It is not the rubber polymers alone that give elastomeric materials their special elastomeric properties, but the combination of crosslinked macromolecules and solid, reinforcing nanoscale filler particles that confer these outstanding characteristic profiles to modern rubber parts for a multitude of applications. Any industrially used rubber can, therefore, be considered a nanocomposite material.

This special issue of *Advances in Polymer Science*, "Designing of Elastomer Nanocomposites: From Theory to Applications," is dedicated to Gert Heinrich, one of the great researchers in the field of elastomeric materials, on the occasion of his 65th birthday.

The first chapter of this book is devoted to the non-affine tube model of rubber elasticity, derived by Gert Heinrich during his time in Merseburg. The model has been extended to account for the finite extensibility of network chains and implemented into a finite element code. Various engineering applications of this model are reviewed by Behnke and Kaliske.

The reinforcement of rubber is examined in terms of filler network dynamics at small strains in the chapter by Tunnicliffe and Busfield. The concepts of filler networking, breakage, Payne effect, and physical ageing are discussed in the context of thermoviscoelasticity and taken as the basis for explanation of results for filled systems.

Persson et al. contribute a chapter on the contact mechanics, friction, and adhesion of rubber at rough surfaces. Using the approach of multiscale contact mechanics, the authors discuss different important practical applications such as the leak rate of static seals and the friction force of dynamics seals, as well as friction experiments and the interpretation of the resulting friction coefficients in dry and lubricated states.

A multiscale approach for the modeling of dynamic-mechanical properties of unfilled and filled elastomers is presented in the chapter by Ivaneiko et al. The proposed theoretical approach allows simultaneous and precise modeling of the frequency dependence of the dynamic-mechanical moduli of elastomer nanocomposites across a broad frequency domain, giving so-called master curves.

Not only rubbers show viscoelastic behavior, these properties are also of great importance in our daily food. Zielbauer, Vilgis et al. investigate network theories for unfilled and filled rubbers and compare these soft materials with the structure and properties of food systems. The common points between elastic materials and food gels are fundamentally discussed and the close connections are explained.

Most rubber materials are crosslinked by covalent bonds. However, Basu et al. give a review of elastomers that are crosslinked by a different mechanism. Nanostructured ionomeric elastomers show fascinating properties; maybe one of the most impressive examples is the self-healing ability of some of these rubbers.

Modern nanoparticles are very promising filler particles for novel elastomeric nanocomposites, providing outstanding features. Graphene is the youngest member of the carbon allotrope family and is sometimes referred to as the mother of all carbon nanomaterials. Two contributions in this issue of *Advances in Polymer Science* deal with this nanofiller system. Mondal et al. describe techniques for functionalization of graphene-like nanofillers by means of small molecules and macromolecules. Different strategies, in particular mixing in latex, solution mixing, and melt mixing, are introduced and the morphology and physical properties of the obtained graphene-based elastomeric nanocomposites are presented. The chapter by Klüppel et al. gives an overview of the potential of nanocomposites based on graphene nanoplatelets and their hybrid systems with industrial fillers. A variety of different application-oriented experimental methods such as static gas adsorption, gas permeation measurements, fracture mechanics, and friction experiments show the potential of these new materials for different purposes.

The fracture of materials is mostly an undesirable process that dramatically reduces the service life of structural components. Stoček et al. review advanced experimental methods for characterizing crack initiation in technical rubbers, crack propagation, and rubber wear under practical loading conditions.

Finally, we would personally like to express our thanks for the time, passion, and energy devoted by all contributing authors, from both academia and industry. Also very deserving of thanks are the reviewers for their excellent service and feedback, as well as the editorial team of *Advances in Polymer Science*, who assisted all of us through the editing and processing of manuscripts.

We are confident that the readers of this volume will find valuable and useful information on various aspects of such a fascinating material as elastomeric nanocomposites.

Dresden, Germany — Klaus Werner Stöckelhuber
Dresden, Germany and Tampere, Finland — Amit Das
Hanover, Germany — Manfred Klüppel

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