

Editors

Sajid Alavi, PhD

Sabu Thomas, PhD

K. P. Sandeep, PhD

Nandakumar Kalarikkal, PhD

Jini Varghese

Srinivasarao Yaragalla

Apple Academic Press



POLYMERS FOR PACKAGING APPLICATIONS

Edited by

Sajid Alavi, PhD, Sabu Thomas, PhD, K. P. Sandeep, PhD, Nandakumar Kalarikkal, PhD, Jini Varghese, and Srinivasarao Yaragalla



Apple Academic Press Inc. 1 3333 Mistwell Crescent Oakville, ON L6L 0A2 Canada

Apple Academic Press Inc. 9 Spinnaker Way Waretown, NJ 08758

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International Standard Book Number-13: 978-1-926895-77-2 (Hardcover)

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Library of Congress Control Number: 2014940534

Library and Archives Canada Cataloguing in Publication

Polymers for packaging applications/editors: Sajid Alavi, PhD, Sabu Thomas, PhD, K.P. Sandeep, PhD, Nandakumar Kalarikkal, PhD, Jini Varghese, and Srinivasarao Yaragalla.

Includes bibliographical references and index.

ISBN 978-1-926895-77-2 (bound)

- 1. Food--Packaging. 2. Polymers. 3. Plastics. 4. Polymers--Biodegradation.
- 5. Plastics--Biodegradation. 6. Nanocomposites (Materials)--Biodegradation.
- 7. Food--Packaging--Technological innovations. I. Alavi, Sajid, author, editor II. Thomas, Sabu, editor III. Sandeep, K. P., author, editor IV. Kalarikkal, Nandakumar, editor V. Varghese, Jini, editor VI. Yaragalla, Srinivasarao, editor

TP374.P64 2014

664' 09

C2014-903401-6

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POLYMERS FOR PACKAGING APPLICATIONS

ABOUT THE EDITORS

Sajid Alavi, PhD

Sajid Alavi, PhD, is a Professor of Extrusion Processing and Food Engineering in the Department of Grain Science and Industry at Kansas State University, Manhattan, Kansas, USA. He received his BS degree (1995) in Agricultural Engineering from Indian Institute of Technology (Kharagpur), MS (1997) in Agricultural and Biological Engineering from the Pennsylvania State University, and PhD (2002) in Food Science/ Food Engineering from Cornell University, Ithaca, New York. Dr. Alavi's research activities are focused in the areas of food engineering, extrusion processing for industrial and food applications, nanocomposites for packaging applications, mathematical modeling of flow and structure formation in biopolymer melts during extrusion, food microstructure imaging, structure-texture relationships, and new approaches to global food security and nutrition through processing. He has secured over \$6.3 million in extramural funding from various federal, state, and industrial sponsors for his research program. He has supervised seven PhD and 13 Masters level students. Dr. Alavi's received the coveted 2010 Young Research Scientist Award from AACC International, formerly the American Association of Cereal Chemists, which is an important recognition for research accomplishments.

Dr. Alavi designs technology and R&D solutions for numerous food, feed and pet food processors, and is involved in processing and food aid related projects in USA, Africa, India, and other countries around the world. He has been invited to speak at numerous international forums and institutions in USA, Italy, South Africa, Brazil, India, Mozambique, and China. He has provided training and networking opportunities to 800 industry leaders from 30 countries spanning all six continents through his internationally reputed short course "Extrusion Processing: Technology and Commercialization" and similar offerings and workshops in other countries such as India, Brazil and Mozambique.

Sabu Thomas, PhD

Sabu Thomas, PhD, is a Professor of Polymer Science and Engineering at the School of Chemical Sciences and Director of the International and Inter University Centre for Nanoscience and Nanotechnology at Mahatma Gandhi University, Kottayam, Kerala, India. He received his BSc degree (1980) in Chemistry from the University of Kerala, BTech. (1983) in Polymer Science and Rubber Technology from the Cochin University of Science and Technology, and PhD (1987) in Polymer Engineering from the Indian Institute of Technology, Kharagpur. The research activities of Professor Thomas include surfaces and interfaces in multiphase polymer blend and composite systems, phase separation in polymer blends, compatibilization of immiscible polymer

blends, thermoplastic elastomers, phase transitions in polymers, nanostructured polymer blends, macro-, micro- and nanocomposites, polymer rheology, recycling, reactive extrusion, processing—morphology—property relationships in multiphase polymer systems, double networking of elastomers, natural fibers and green composites, rubber vulcanization, interpenetrating polymer networks, diffusion and transport and polymer scaffolds for tissue engineering. He has supervised 64 PhD theses, 30 MPhil theses, and 40 Masters theses. He has three patents to his credit. He also received the coveted Sukumar Maithy Award for the best polymer researcher in the country for the year 2008. Very recently Professor Thomas received the MRSI and CRSI medals for his excellent work. With over 600 publications to his credit and over 15,000 citations, with an h-index of 65, Dr. Thomas has been ranked fifth in India as one of the most productive scientists.

K. P. Sandeep, PhD

K. P. Sandeep, PhD, is a Professor of Food Engineering, Research Leader and Associate Head in the Department of Food, Bioprocessing and Nutrition Sciences as well as an associate faculty member in the Department of Biological and Agricultural Engineering at North Carolina State University, Raleigh, North Carolina, USA. He is also Site Director of the Center for Advanced Processing and Packaging Studies. He received his BS degree (1991) in Agricultural Engineering from the Indian Institute of Technology (Kharagpur), his MS (1993), and his PhD (1996) in Agricultural and Biological Engineering from the Pennsylvania State University. His research areas include nanotechnology, thermal and aseptic processing, continuous flow microwave processing, heat exchanger design, development of sensors, mathematical modeling of fluid flow and heat transfer, microelectromechanical systems (MEMS), and nuclear magnetic resonance (NMR). Dr. Sandeep has co-authored scores of books, peerreviewed publications, and technical abstracts, posters, and presentations on aseptic processing and related topics. He has served as a consultant to several companies and serves as a member of the advisory board to the Southeast Dairy Foods Research Center. He also conducts short courses tailored to meet the specific needs of industry on topics such as nanotechnology, thermal processing and NMR.

Nandakumar Kalarikkal, PhD

Dr. Nandakumar Kalarikkal is a Professor of Physics at the School of Pure and Applied Physics and Joint Director of International and Inter University Centre for Nanoscience and Nanotechnology at Mahatma Gandhi University, Kottayam, Kerala, India. He received his BSc degree (1984) in Physics from Calicut University, and MSc (1986) and PhD (1992) in Physics from Cochin University of Science and Technology, Kerala, India. His research activities involve nanotechnology and nanomaterials, sol-gel synthesis of nanosystems, semiconducting glasses, ferroelectric ceramics, and nonlinear and electro-optic materials. He is the recipient of research fellowships and associateships from prestigious organizations such as the Department of Science and Technology and Council of Scientific and Industrial Research of the Government of India. He has collaborated with national and international scientific institutions

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in India, South Africa, Slovenia, Canada, and Australia, and is co-author of several books chapters, peer-reviewed publications, and invited presentations in international forums.

Jini Varghese

Ms. Jini Varghese is currently a Research Scholar at the School of Chemical Sciences at Mahatma Gandhi University, Kottayam, Kerala, India. She is engaged in doctoral studies in the area of EPDM rubber-graphene nanocomposites. She received her MSc degree in Analytical Chemistry from Mahatma Gandhi University. Ms. Varghese is a recipient of the Women Scientist Award from the Department of Science and Technology of the Government of India.

Srinivasarao Yaragalla

Mr. Srinivasarao Yaragalla is a Research Scholar at the International and Inter University Centre for Nanoscience and Nanotechnology at Mahatma Gandhi University, Kottayam, Kerala, India. He is engaged in doctoral studies in the area of graphene-based polymer nanocomposites. He has also conducted research work at the Universiti Teknologi MARA in Malaysia. In 2010, Mr. Yaragalla received a prestigious research fellowship administered jointly by the Council of Scientific and Industrial Research and University Grants Commission of the Government of India.

LIST OF CONTRIBUTORS

Boussad Abbès

University of Reims Champagne-Ardenne, GRESPI/MPSE, Campus Moulin de la Housse, BP 1039, 51687 REIMS Cedex 2, France.

Email: boussad.abbes@univ-reims.fr

Fazilav Abbès

University of Reims Champagne-Ardenne, GRESPI/MPSE, Campus Moulin de la Housse, BP 1039, 51687 REIMS Cedex 2, France.

S. Alavi

Department of Grain Science & Industry, Kansas State University, 201 Shellenberger Hall, Manhattan, KS 66506, U.S.A.

Email: salavi@k-state.edu

C. Anandharamakrishnan

Department of Food Engineering, CSIR - Central Food Technological Research Institute, Mysore - 570 020, India.

Email: anandharamakrishnan@cftri.res.in

D. Sarayana Bayan

Department of Mechanical Engineering, National Institute of Technology Karnataka, Mangalore – 575 025, India

Email: saranbav@gmail.com

Umesh Bhardwaj

Department of Chemical Engineering, Indian Institute of Technology Guwahati-781 039, Assam, India.

Dr. J. Bindu

Fish Processing Division, Central Institute of Fisheries Technology, Cochin 682 029, Kerala, India. Email: bindujaganath@gmail.com

Sanjava K. Dash

Orissa University of Agriculture and Technology, Department of Agricultural Processing and Food Engineering, Bhubaneswar, Odisha, India.

Email: sk dash1006@hotmail.com

S. D. Deshpande

Central Institute of Agricultural Engineering, Nabi Bagh, Berasia Road, Bhopal – 462 016, Madhya Pradesh, India.

Email: sdd1953@gmail.com

Prodyut Dhar

Department of Chemical Engineering, Indian Institute of Technology Guwahati-781 039, Assam, India.

Surendra S. Gaur

Indian Institute of Technology Guwahati, Department of Chemical Engineering, Guwahat - 781 039, Assam, India.

Dr. T. K. Srinivasa Gopal

Central Institute of Fisheries Technology, Cochin 682 029, Kerala, India

Email: tksgopal@gmail.com

Ying-Qiao Guo

University of Reims Champagne-Ardenne, GRESPI/MPSE, Campus Moulin de la Housse, BP 1039, 51687 REIMS Cedex 2, France.

P. P. Kanekar

Microbial Sciences Division, MACS' Agharkar Research Institute, G. G. Agarkar Road, Pune – 411 004, Maharashtra, India.

Email: kanekarpp@gmail.com

S. P. Kanekar

Microbial Sciences Division, MACS' Agharkar Research Institute, G. G. Agarkar Road, Pune - 411 004, Maharashtra, India

Vimal Katiyar

Indian Institute of Technology Guwahati, Department of Chemical Engineering, Guwahati - 781 039, Assam, India.

Email: vkatiyar@iitg.ernet.in

Usha Kiran Kolli

Department of Food Engineering, CSIR - Central Food Technological Research Institute, Mysore, Karnataka - 570 020, India.

S. B. Kondawar

1R.T.M. Nagpur University, Department of Physics, Polymer Nanotech Laboratory, University Campus, Amravati Road, Nagpur-440033, Maharashtra, India.

Email: sbkondawar@yahoo.co.in

Prakash Kotecha

Department of Chemical Engineering, Indian Institute of Technology Guwahati - 781 039, Assam, India

P. R. Kshirsagar

Microbial Sciences Division, MACS' Agharkar Research Institute, G. G. Agarkar Road, Pune – 411 004, Maharashtra, India.

Amit Kumar

Indian Institute of Technology Guwahati, Department of Chemical Engineering, Guwahati – 781 039, Assam, India.

Dr. P. Kumar

Department of Food, Bioprocessing, and Nutrition Sciences, North Carolina State University, Raleigh, NC.

S. O. Kulkarni

Microbial Sciences Division, MACS' Agharkar Research Institute, G. G. Agarkar Road, Pune – 411 004, Maharashtra, India.

G. C. Mohan Kumar

 $\label{eq:continuous} Department of Mechanical Engineering, National Institute of Technology Karnataka Srinivasnagar, Surathkal, Mangalore - 575025, Karnataka, India.$

Zhigang Liu

Department of Packaging Engineering, Jiangnan University, Wuxi, 214122, China Email: liuzg@jiangnan.edu.cn

Lixin Lu

Department of Packaging Engineering, Jiangnan University, Wuxi, 214122, China.

Dr. A. K. Mallick

Export Inspection Agency, 6th Floor CMDA Tower II, No: 1, Gandhi Irwin Road, Egmore, Chennai - 600 008

Email: arunakumarmallick@gmail.com

S. S. Nilegaonkar

Microbial Sciences Division, MACS' Agharkar Research Institute, G. G. Agarkar Road, Pune – 411 004, Maharashtra,

Rahul Patwa

Department of Chemical Engineering, Indian Institute of Technology Guwahati - 781 039, Assam, India.

Akhilesh K. Pal

Department of Chemical Engineering, Indian Institute of Technology, Guwahati - 781 039, Assam, India.

M. Ponraj

Microbial Sciences Division, MACS' Agharkar Research Institute, G. G. Agarkar Road, Pune – 411 004, Maharashtra,

Dr. C. N. Ravishankar

Fish Processing Division, Central Institute of Fisheries Technology, Cochin 682029, Kerala, India Email: Cnrs2000@gmail.com

K. P. Sandeep

Department of Food, Bioprocessing, and Nutrition Sciences, North Carolina State University, Raleigh, NC. Email: kp_sandeep@ncsu.edu

S. S. Sarnaik

Microbial Sciences Division, MACS' Agharkar Research Institute, G. G. Agarkar Road, Pune – 411 004, Maharashtra,

Rungsinee Sothornvit

Department of Food Engineering/Faculty of Engineering at Kamphaengsaen/PHTIC Email: fengrns@ku.ac.th

S. K. Srivastava

School of Biochemical Engineering, Institute of Technology, Banaras Hindu University, Varanasi - 221005, Uttar Pradesh, India.

Panuwat Suppakul

Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, 50 Ngamwongwan Rd., Ladyao, Chatuchak, Bangkok, Thailand 10900. Email: fagipas@ku.ac.th

X. Z. Tang

College of Food Science and Engineering, Nanjing University of Finance & Economics, Nanjing, Jiangsu Province, 210046, China.

Abhishek Dutt Tripathi

Centre of Food Science and Technology, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi - 221005, Uttar Pradesh, India.

Email: abhi itbhu80@rediffmail.com

Neelima Tripathi

Department of Chemical Engineering, Indian Institute of Technology Guwahati - 781 039, Assam, India.

V. D. Truong

U.S. Dept. of Agriculture, Agricultural Research Service, South Atlantic Area, Food Science Research Unit, Raleigh, NC 27695, U.S.A.

Zhiwei Wang

Packaging Engineering Institute, Jinan University, Guangzhou, Guangdong 510632, China.

Ajay Yaday

Centre of Food Science and Technology, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi - 221005, Uttar Pradesh, India.

LIST OF ABBREVIATIONS

AAGR 8Average annual growth rate
ADC Analog to digital convertor
AFM Atomic force microscope
ATR Attenuated total reflectance

BC Bacterial cellulose
BSEs Back-scattered electrons

CAP Controlled-atmosphere packaging CAS Controlled atmosphere storage

CSIR Council for Scientific and Industrial Research

CSLM Confocal scanning laser microscope
DMTA Dynamic mechanical thermal analysis
DRS Dielectric relaxation spectroscopy
DSC Differential scanning calorimeter
DTA Differential thermal analysis
EELS Electron energy loss spectroscopy

EM Elastic modulus

EMI Electromagnetic interference
EPA Environmental protection agency
ERH Equilibrium relative humidity
FDA Food and drug administration
FDM Finite difference method
FEA Finite element analysis
FIB Focused ion beam

FID Flame ionization detector FSI Food spoilage indicator FSL Food-simulating liquids

FTIR Fourier transforms infra-red spectroscopy
GC-MS Gas chromatography-mass spectrometry

GFSE Grape fruit seed extracts

GPC Gel permeation chromatography
HDPE High density polyethylene
HIPS High impact polystyrene

HPLC High-performance liquid chromatography

ICI Imperial chemical industry

ICP-MS Inductively coupled plasma-mass spectrometry

ICPs Intrinsically conductive polymers
IFT Institute of Food Technologists

ILT Ideal laminate theory LCA Life cycle assessment

LDH Layered double hydroxide
LEO Lemongrass essential oil
LLE Liquid—liquid extraction
LMIS liquid metal ion source
LWA Liquid water absorption

MAP Modified atmosphere packaging

MWNT Multi-walled nanotubes NCF Nanocellulose fibers

NIAS Non-intentionally added substances

NMR Nuclear magnetic resonance
NNI National nanotech initiative
OML Overall migration limit

OMLS Organically modified layered silicate

OP Oxygen permeability
OTR Oxygen transmission rate
PCNC Polymer—clay nanocomposites
PNCs Polymer nanocomposites
RFID Radio frequency identification

RH Relative humidity

SEM Scanning electron microscope SML Specific migration limit

SPI Soy protein isolate

SPM Scanning probe microscope STM Scanning tunneling microscope

SWNT Single-wall nanotube

TEM Transmission electron microscope

TEMAP Thermally equilibrious modified atmosphere packaging

TEMT Transmission electron microtomography

TPS Thermoplastic starch
TS Tensile strength

UPC Universal Product Code

VARTM Vacuum assisted resin transfer molding

VRH Variable range hopping WAXS Wide-angle X-ray scattering

WPI Whey protein isolate
WVP Water vapor permeability
WVTR Water vapor transmission rate

XRD X-ray diffraction

PREFACE

The world-wide market for plastic films and sheets used in various packaging and non-packaging applications exceeds \$100 billion and is growing at an annual rate higher than the global gross domestic product. The polymeric materials that are used include low and high density polyethylene, polyethylene terephthalate, biaxially oriented polypropylene, copolymer polypropylene, poly(vinyl chloride) and ethylene vinyl alcohol. No doubt this massive usage of plastics is driven by several benefits including convenience and economics, but the drawbacks are also becoming apparent.

Plastics do not biodegrade, primarily because they are made of synthetic polymers and no microbe has yet evolved that can feed on them. Disposal of the millions of tons of plastic waste generated every year takes up huge areas in the form of landfills. Plastic polymers may not be toxic themselves but the myriad of chemical monomers added to them for improving their properties can be released to the surroundings and contact materials over time or under conditions such as heat and exposure to sunlight or photodegradation. An example is bisphenol A or BPA that is added as a plasticizer but banned for use in applications involving packaging or containers for infant food due to its potential toxic effects. Waste plastics can also attract and accumulate chemical poisons present in the environment such as water contaminated with DDT and PCB. A striking example of the problem with plastic waste is the 'The Great Pacific Garbage Patch' covering an area roughly the twice the size of France in the Pacific Ocean*. The combined weight of plastic accumulated in this 10-meter deep plastic soup is estimated at three million tons and increasing steadily due to several major sea currents converging to this region that bring flotsam from the Pacific coasts of Southeast Asia, North America, Canada and Mexico. Its toxic effect on marine life is just beginning to be understood.

In this backdrop, the development and use of bio-based and/ or biodegradable polymers is gaining importance. Polylactic acid, polyvinyl alcohol and polybutylene succinate are plastic materials that can be decomposed by bacteria or other living organisms. These materials often lack the performance characteristics, such as strength, flame retardance or barrier properties, of conventional plastics but they can be enhanced by using various nanofillers. Research on such nanocomposites is also gaining widespread attention.

Developments in the above mentioned areas were focus of the International Conference on Polymers for Packaging Applications (ICPPA 2012) organized at Mahatma Gandhi University in Kottayam, India from March 31st to April 2nd, 2012. Scientists from the U.S.A., U.K., France, China, Thailand, Malaysia, Iran and India presented cutting edge research in the areas of food, non-food, and industrial packaging applications of polymers, blends, nanostructured materials, macro, micro and nanocomposites, and renewable and biodegradable materials. This book and its focus have origins in the aforementioned international conference. Several of the speakers at ICPPA 2012

contributed to the various chapters. Due to reasons related to sustainability, recycling and regulatory issues, the topics discussed in the conference and ongoing research has gained even greater urgency in the last two years.

This book emphasizes interdisciplinary research on processing, morphology, structure, and properties as well as applications of polymers in packaging of food and industrial products. It is useful for chemists, materials scientists and food technologists. It details physical, mechanical, electrical and barrier properties of polymers and biopolymers, as well as sustainability, recycling, and regulatory issues. The book contains a good mix of review chapters and experimental studies, and is divided into four major sections. Chapters in the first section provide an overview of traditional plastics in packaging applications including a specific example related to food packaging. Additives used for improving properties of plastics are described along with experimental studies on their migration. The second section focuses on biopolymers and biodegradable plastics, and their synthesis, commercial production, properties and use in packaging of food and industrial products and biomedical applications. Recycling and life cycle analysis for plastics and bioplastics is also discussed. The next section contains chapters related to nanotechnology and bio-nanocomposites in packaging applications. Various nanofillers, including phyllosilicates, metallic nanofillers, carbon nanotubes and graphene, are described and also regulatory issues discussed. Analytical techniques and approaches based on mathematical modeling are presented for understanding the structure, and barrier and mechanical properties of bio-nanocomposites. The final section has chapters describing the state-of-the-art in modified atmosphere packaging for foods, and innovations related to active and intelligent packaging. The last chapter presents an intriguing concept of conductive polymers for functions such as electromagnetic shielding and active packaging.

The editors have made a conscious effort to select authors from various parts of the world representing diverse disciplines including material science, physics, packaging engineering, microbial sciences and food technology. We would like to thank them profusely for their high quality submissions and contributing to this truly multi-disciplinary effort. Special thanks to our readers, and the editorial staff of Apple Academy, Inc. for their assistance and helpful suggestions at every step.

 Sajid Alavi, PhD, Sabu Thomas, PhD, K. P. Sandeep, PhD, Nandakumar Kalarikkal, PhD, Jini Varghese, and Srinivasarao Yaragalla

* Moore, C. J., Moore, S. L., Leecaster, M. K., and Weisberg, S. B. 2001. Marine Pollution Bulletin 42 (12) 1297–300.