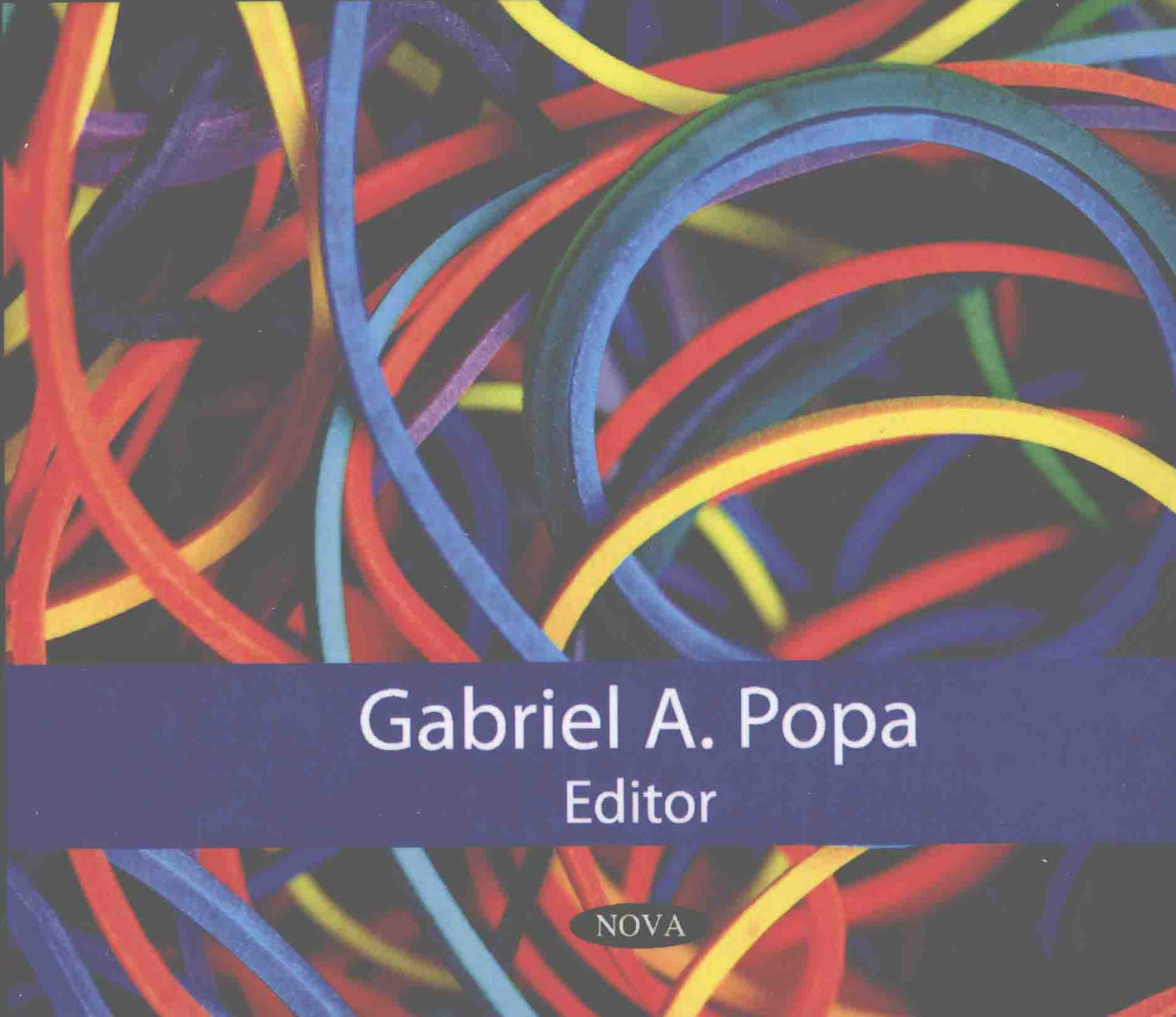
MATERIALS SCIENCE AND TECHNOLOGIES

RUBBER

Types, Properties and Uses



Gabriel A. Popa
Editor

NOVA

MATERIALS SCIENCE AND TECHNOLOGIES

RUBBER: TYPES, PROPERTIES AND USES

GABRIEL A. POPA
EDITOR

Nova Science Publishers, Inc.
New York

Copyright © 2011 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
Rubber : types, properties, and uses / editor, Gabriel A. Popa.
p. cm.
Includes index.
ISBN 978-1-61761-464-4 (hardcover)
1. Rubber. I. Popa, Gabriel A.
TA455.R8R835 2010
620.1'94--dc22
2010031353

Published by Nova Science Publishers, Inc. † New York

MATERIALS SCIENCE AND TECHNOLOGIES

RUBBER: TYPES, PROPERTIES AND USES

PREFACE

Natural rubber is an elastomer that was originally derived from a milky colloidal suspension, or latex, found in the sap of some plants. Rubber's usefulness is based on the unique elasticity of its constituent polymer molecules, which are capable of returning to their original coiled shape after being stretched to great extents. The use of rubber is widespread, ranging from household to industrial products. This book presents topical research in the study of rubber, including the mechanical behavior of elastomers; blends of epoxidized natural rubber and thermoplastics; recycled rubber and the use of scrap rubber tires; use of isocyanate as a primer for synthetic rubber; steam thermolysis of technical rubber material; and the structure of elastomers.

Chapter 1 - Crosslinking or curing, forming covalent, hydrogen or other bonds between polymer molecules, is a common technique to improve polymer properties.

The first method of curing (crosslinking) refers to Charles Goodyear in 1839 when he cured natural rubber with elemental sulfur in high temperature. Although the vulcanization time was more than 5 hours.

Since that date, vulcanization process had massive improvement. In fact except elemental sulfur, huge numbers of curing agents distinguished. In addition to natural rubber (NR), so many other synthesized rubbers (SR), cured as well.

In a cure system recipe, several ingredients participated including polymer (rubber), reinforcement agent (filler), accelerator, activator, anti aging, processing oil and etc.

For many uses, even vulcanized rubbers do not exhibit satisfactory mechanical properties, including tensile strength, stiffness (hardness), abrasion resistance, and tear resistance. Fortunately, these properties can be enhanced by the addition of certain fillers to the rubber before vulcanization (curing). In fact, most usage of elastomers would be impossible without the reinforcing character of certain fillers, such as carbon blacks and structured silica. With an implicit reference to tire technology, *reinforcement* is usually defined as the ‘improvement in abrasion, tear, cutting and rupture resistance, in stiffness and hardness of vulcanized compounds through the incorporation of finely divided (mineral) particles’ Fillers for rubber can be divided into two classes, inert fillers, such as clay, whiting and barites, which make the rubber mixture easier to handle before vulcanization but have little effect on its physical properties; and reinforcing fillers, which do improve the above named unsatisfactory properties of the vulcanised rubber. Carbon black and silica are in latter category. In fact vulcanization restrains the long-range movements of the polymer molecules but leaves their local segmental mobility. High reinforcement stiffens the mass and improves its toughness by restricting this local freedom of movement.

Chapter 2 - Besides classical construction materials, polymers and elastomers find nowadays a wide use in the design of mechanical components and systems and in many industrial applications. The reasons are their economy and their peculiar characteristics that fit with specific applications where traditional materials fail. Elastomers show complex mechanical and rheological behaviors. They are able to reach very large deformations before rupture, with small residual strain after load removal; furthermore, the relationship between stress and strain is strongly non-linear.

The constitutive models frequently used to describe this behavior are referred to as hyperelastic; they are based on the definition of a specific strain energy potential, that is a function of principal strains. Principal stresses can be calculated by derivation of this potential. The hyperelasticity is affected in almost all elastomers by several inelastic phenomena, like permanent set, hysteresis in cyclic loading conditions, and a particular damage effect, called “Mullins effect”.

Another typical characteristic of elastomers is the viscous behavior. While hyperelastic and pseudo-elastic models refer to quasi-static loading of the material, it is experimentally clear that rubbers have time-dependent mechanical properties, showing relevant creep and relaxation phenomena; moreover, their elastic and damping moduli are functions of the frequency of the solicitation. Indeed, several models for both linear and non-linear visco-elasticity have been developed and proposed in literature.

All the mechanical behaviors mentioned above are the object of the present dissertation, where a comparison of principal numerical models available in literature is given.

Suitable experimental rigs and techniques have been adopted in order to perform experimental tests with different strain and stress conditions, such as uniaxial, planar and equal-biaxial. When necessary, the strain distributions of the specimens have been evaluated by optical full-field techniques based on digital image processing.

Many examples of model parameters identification (hyperelastic, pseudo-elastic, viscoelastic) are given for Styrene-Butadiene rubbers starting from the experimental data collected. In addition to standard procedures for inverse problems mainly based on the “model updating” concept, the application of the “Virtual Fields Method” has been investigated in the characterization of hyperelastic models from planar tension tests. In all the work, a particular remark is given to the multiaxial approach: the experimental data collected from different kinds of tests are involved jointly in the inverse procedure for model calibration (uniaxial, planar, equibiaxial). This approach is shown to provide reliable material parameters, which ensure stable results in FEM simulations and can be transferred into analyses of generic loading conditions.

Chapter 3 - The pure rubber appears under milky liquid aspect called latex. It comes from Hevea tree and its industrial development started with the sulphur vulcanisation process discover by Charles Goodyear in 1840. The development of synthetic rubber-like materials or elastomers started eighteen years later. Thus, butadiene copolymer and Styrene Butadiene Rubber were elaborated between 1920 and 1930, and thermoplastic elastomers were synthesised between 1950 and 1960.

Defining the reliability of rubbers is an essential step before designing or dimensioning parts of such materials. Thus, analysing properties, behaviour and fracture of elastomers should represent, without doubt, an interesting work since there is a strong need in industry to well control performances of these materials and to clearly understand their failure process. In fact, on the one hand, any knowledge in this domain could contribute in reducing the development and the qualification cycles requiring a significant financial investment and very long delays. On the other hand, the mastering of designing techniques should improve the quality, the safety and the reliability of structure containing rubber parts.

Elastomers exhibit strong mechanical properties like, among others, high deformation before failure, good shock resistance and reasonable fatigue lifetime. Such properties make these materials so attractive. In fact, they are progressively more used in many engineering industries in components of machines, vehicles and structures, as soon as in everyday life. However, demands on their performance are continually rising.

Rubbers have complex microstructures, which become even more complex in the case of compounds with other components. In order to extend their application fields, these materials are generally reinforced by fillers, often carbon black or silica, and they must undergo a composite chemical process of cross-linking, by which their long, entangled molecules are covalently linked to form a three-dimensional network. Moreover, rubbers are affected by environmental conditions like mechanical loading, temperature variation, thermal and chemical aging… The morphology of the final product makes it difficult to accurately predict the properties and the mechanical behaviour of the material. Nevertheless, it is known that this behaviour includes hyperelasticity (elasticity and large deformation), non-linearity, viscosity (strain-rate-dependence), hysteresis, stress softening (Mullins effect). So, describing such behaviour is not easier, but particularly challenging as well. This challenge has attracted extensive research attention since the pioneer work of Mooney (1940). Indeed, several authors developed numerous models to describe mechanical behaviours of rubbers or more largely those of amorphous polymers. The majority of these models is based on a phenomenological approach. Nevertheless, some models based on the microscopic response of network polymer chains have appeared in the last two decades.

Beyond the knowledge of their properties and their behaviour, evaluation of the performance of elastomers to resist to the fracture is interesting from both the scientific point of view and the application point of view. Hence, it is necessary to develop procedures that allow an exact determination of a fracture criterion (fracture toughness) of these materials. Although, large investigations are developed in the literature about this subject, no fracture robust unified criterion exists neither under monotonic loading nor under cyclic loading. To avoid series of test on prototypes, rubber components are therefore often oversized.

This work represents a literature review on properties, behaviour and fracture of elastomers under monotonic and cyclical loadings. Because of the wide diversity of rubber-like materials and the extensive range of their application, it is difficult to oversee all areas of interest. Therefore, this chapter gives, firstly, a brief overview of principal properties of such materials, then summarises their mechanical behaviour models and, finally, develops more widely concepts dealing with their fracture. A particular attention will be paid to phenomenological approaches.

Chapter 4 - Electric elastomer, a type of an artificial muscle, have been extensively investigated in the last decade. These responsive materials are broadly classified as electronic or ionic according to its operational mechanism. In this report, our group's results are summary. In the ionic group, two kinds of nature polyelectrolyte hydrogels, gelatin hydrogel and gelatin/alginate semi-interpenetrating polymer network membranes, were prepared. It is found that in a neutral NaCl solution, the hydrogels bend toward the cathode under a non-contact DC electric fields. Under a cyclically varying electric field, the hydrogels exhibit a good reversible bending behavior. In addtion, an electric-stimulus-response of the gelatin hydrogel in the medium of silicone oil was also explored. In the electronic group, based on Gelatin and silicone rubber as the matrix, two types of electric elastomers, Barium Titanate/Gelatin and starch/gelatin/glycerin composite Hydrogel Elastomers, were prepared without and with a curing electric field, respectively. The results suggest that the particles were aligned in the matrix under an curing DC electric field. It is suggested that their mechanical property is controlled by an applied electric field and the weight fraction of particles. On the other hand, two types of starch/ silicone oil /silicone rubber electric elastomers were also prepared in the absence and presence of a curing electric field, respectively. Silicone oil reduces the viscosity of the silicone rubber prepolymer, and then the electric field-induced storage modulus becomes larger. Furthermore, a transformer oil keeping a liquid phase in the whole curing process was added, and starch/ transformer oil drop/silicone rubber hybrid elastomer was prepare. The larger storage modulus sensitivity was obtained. Smart electric elastomer will be extensively applied in artificial muscles and electric actuators.

Chapter 5 - This review article deals with the different types of rubber, their properties and uses. Brief description of the various rubber processes and ingredients used for the preparation of the final rubber products is given. The last part of the article is devoted to rubber composites and nanocomposites describing rubber/carbon nanotubes, rubber/nanoclays and rubber/nano metals.

Chapter 6 - Epoxidized natural rubber (ENR) is chemically modified natural rubber. When blended with crystalline thermoplastic polymers, immiscible systems result. Properties of those systems are ruled by the relative amount of the constituents and the distribution of phases in the alloy. Thermal behavior governs development of morphologies by a delicate balance between rate of crystallization and mobility of the elastomer phase. In blends where the crystalline constituent is in excess, this component crystallizes out from the melt comprising a dispersion of ENR domains. At the opposite side of the composition scale, ENR being in excess, crystalline domains will develop in the ENR matrix. In the chapter, we focus dominantly on three aspects: thermal properties and morphology of elastomer thermoplastic blends. It embraces melting and crystallization behavior in those blends and their influence on morphology development. The authors follow also the question: Do these blend systems become candidates for polymer electrolytes when one adds salt? In what way is the salt distributed between the blend components? These are crucial fundamental problems and it seems worthwhile to elucidate them. Melt reactions with (hydroxy alkanoate) polymers as well as grafting of ENR chains offer possibilities of manipulating blend morphologies. This might be favorable also for the electrical properties of the salt-polymer blend solutions.

Chapter 7 - The chapter deals with the characterization and the mechanical properties of natural rubber latex (NRL) / Chitosan (CS) blends. Chitosan has been blended with natural rubber latex by solution casting method followed by compression molding. The blend is found to be incompatible from DSC, morphology and FTIR studies. Blending has improved the thermal properties of chitosan and the environmental stability and antifungal properties of NR. The blended samples show enhanced mechanical properties. Aging of natural rubber/chitosan blends at 55 0C for 10 days increased the tensile strength due to thermal cross-linking in the natural rubber phase. Improvement in the mechanical properties is explained in terms of interfacial adhesion between the two phases, due to the interfacial interaction between NRL and CS and also due to thermal cross-linking of NR during compression. The fraction of bound rubber and undissolved chitosan indicates that there is interfacial interaction between the phases in the blend and also that thermal cross-linking has occurred during compression at 140 0C. Thermal cross-linking and the presence of non rubber constituents of latex are responsible for the modification of interface and improvement in properties.

Vulcanization of rubbery phase in the blend using dicumyl peroxide has resulted in an increase in interfacial adhesion and a finer morphology, hence an increase in tensile strength, hardness and thermal stability and a reduction in solvent penetration.

The blends show improved thermal stability, tensile strength and surface hardness upon compatibilisation with maleic anhydride (MA), due to the formation of modified chitosan/natural rubber in the blend through interaction of maleic anhydride with chitosan and natural rubber. Maleic anhydride grafted NR chain is highly reactive towards the functional group on the chitosan moiety, and while pressing at elevated temperature interaction develops between the maleic anhydride treated NR and chitosan. Since there is only a small amount of water absorption at room temperature and at 100 0C for vulcanized blends, by processing with suitable additives, like TMTD (Tetrametyl thiuram dissulfide), ZnO (Zinc oxide), MBT (Mercapto benzo thiazole) and stearic acid, it can be used for making tanks for preserving water or can be used for steam lanes.

Chapter 8 - Rubber is produced from natural or synthetic sources. Natural rubber is obtained from the milky white fluid called latex, found in many vegetal, while synthetic rubbers are produced from unsaturated hydrocarbons. Natural rubber has been used for commercial vehicles such as lorries, buses and trailers; synthetic rubbers, with specific properties is used for targeted applications, in small lorries, private cars, motorbikes and bicycles. The synthetic rubbers, commonly used for tire manufacturing are styrene-butadiene and/or butadiene rubber. Butyl rubber, since it is gas-impermeable, is commonly used for inner tubes.

There is a large wastage of rubber tires in many countries and the aim of this brief review is to give some ideas on what can be done with this valuable resource. Whether rubber tires are reused, reprocessed or hand crafted into new products, the end result is that there is less waste and less environmental degradation. There are many ways in which tires and inner tubes can be reused or reclaimed. The waste management hierarchy dictates that re-use, recycling and energy recovery, in that order, are superior to disposal and waste management options. Traditional rubber recycling processing paths are outlined in Table 1.

Efforts to develop recycled rubber – plastic blends have followed earlier blending research on pure polymers that produced both thermoplastic elastomers and rubber-toughened plastics. The large interfacial area and particle/filler interaction is modifying the glass transition temperature and mechanical properties.

The end-of-live tires can be recycled and used as a second raw material. The waste tires can be recovered through blending recycled rubber with other materials (organic and inorganic compounds) as an efficient alternative in waste rubber recycling, to obtain composite materials. The rubber can act as matrix in composites and the filler may consist of other (recycled) organics, such as plastic materials, or fillers (inorganics, wood, etc.).

Chapter 9 - Elastomers widely named rubber represent an important family of polymers used in many applications. The field of applications is wide, ranging from household to industrial products. Tires, tubes and flooring are the largest consumers of rubber. As many polymers, they are subjected to different aggressions. In fact, heat and solar radiation in presence of oxygen are the main factor to degrade materials in outdoor applications but we must keep in mind that other agents such as household products, acids, or saline can decrease the sustainability of these materials. In the first approach many scientists focused their attention on the study of the impact of heat or radiations emitted by sun, in presence of atmospheric oxygen, both phenomenon called thermo-oxidation and photo-oxidation, respectively. Depending on the application conditions, one of these mechanisms can predominate. Both processes lead to the degradation of the materials and limit their application and lifetime. So, several investigations are devoted on establishing the mechanism that is behind the degradation of rubber composites and therefore improve their durability.

The following chapter is divided in two parts: the first will concern the use of mass spectrometry to follow the chemical changes during thermo-oxidation of rubbers such as polybutadiene and styrene butadiene rubber. The second part will deal with the effect of photo-oxidation on dyed composites based rubber.

Chapter 10 - The main focus of this chapter is to delve in to the importance and diversity of a thermoplastic elastomer namely styrene butadiene styrene (SBS) block copolymers by investigating its design and subsequent properties. A concise history outlining the development of the material from its earliest reincarnation as styrene butadiene rubber to its ability to be grafted on to hydrogels systems for medical applications will highlight the myriad of potential applications. In exploring the materials architectures, the phase structures between the butadiene and styrene domains will be discussed and an overall account of the morphology and miscibility will be reviewed; while the behaviour of the materials under thermal conditions will be analysed using experimental data. A detailed account of the infra red spectral conditions will be provided, while surface analysis will illustrate the hydrophobicity and subsequent hydrophilicity of SBS and grafted SBS systems respectively. This chapter will also look at the effect of increased crosslinking via ultra violet exposure using thermal analysis.

Chapter 11 - An experimental study of styrene-butadiene rubber (SBR) filled with various content of silica particles with and without surface treatment was done to go ahead in understanding the nature of the rubber reinforcement. Applicability of Klueppel-Schramm model for description of strain softening was evaluated in cyclic loading-unloading tension tests, and parameters of the model as functions of filler volume content were determined. Contribution of viscoelastic effects into the deformation properties of filled rubber was evaluated in creep tests and taken into account for description of strain softening. It is shown that the description of experimental data by Klueppel-Schramm model was considerably improved by taking into account the effect of viscoelasticity.

Chapter 12 - Every year, 800 millions of scrap rubber tires are disposed worldwide as a consequence of the huge increase in the number of vehicles on the road. In the United States alone, about 300 million scrap tires are generated annually and the number is expected to rise by approximately 2% every year. The problem would become more severe due to the rapid growth in domestic consumption in a number of developing countries including China, India, and so forth.

In the past, most scrap tires were dumped in landfills. It is, however, widely agreed that landfilling is not a favorable option considering material loss, land wastage and adverse environmental impacts. In light of these drawbacks, regulations have been laid down in many countries to prevent further landfilling.

To alleviate the problems brought about by scrap tire stockpiles, it is essential to adopt appropriate waste management strategy to cope with the increasing amount of scrap tires generated every year. Major ways of utilizing scrap tires, including retreading, recycling (in civil engineering and ground rubber applications) and energy recovery (e.g. through combustion in cement kilns and pyrolysis) will be reviewed in this chapter. The suitability of these methods will be assessed in terms of sustainability and the associated environmental impacts.

Chapter 13 - A modeling of nanofilled crosslinked rubber using molecular dynamics was introduced, and the effects of the crosslinking density and the strength of filler-polymer interactions on the reinforcement in an elongation simulation were discussed. Filled crosslinked rubber shows reinforcement such as high tensile strength, tear and abrasion resistance. Although the reinforcement of rubber strongly depends on the strength of filler-polymer interaction, the complex physical phenomenon has not been clarified due to the difficulty of analysis by experimental method. In order to clarify the mechanism of reinforcement by filler, a bead-spring model was applied to a crosslinked polymer with nanofillers for coarse-grained molecular dynamics simulation. Two nanofillers connected beads and crosslinked polymer were used as a simulation model. The strength of interactions between nanofiller and polymer based on the Lennard-Jones potential were varied. In order to investigate the effects of crosslinking and nanofiller on reinforcement, uniaxial elongation behavior was studied by coarse-grained molecular dynamics simulation with deformation function. From the uniaxial elongation simulation results and the analysis of polymer dynamics around nanofiller, it was confirmed that the degree of reinforcement depends on the strength of filler-polymer interaction, and one of the factors which influenced the stress was attributed to the existence of a low mobility phase around the nanofiller.

Chapter 14 - CO_2 plasma treatment modifies the surface of VR rubber but due to some ingredients in the rubber formulation that migrate to the adhesive joints preventing adhesion, a reinforcement of the adhesive joint by isocyanate has been considered. Thus, an isocyanate wipe has been performed right after plasma treatment and isocyanate has also been incorporated to the polyurethane adhesive solution. Incorporation of isocyanate to the PU adhesive produces a crosslinking of the urethane groups of the PU adhesive and interlocking with the outermost VR rubber polymeric chains at the interface, which is responsible for the increased adhesion. Application of isocyanate as a primer to the VR rubber surface improves adhesion by reaction of isocyanate at the rubber surface with urethane groups of PU adhesive, creating a crosslinked interface. Thus, wipe of rubber with isocyanate solution in ethyl acetate or incorporation of 4 wt% to the PU adhesive solution enhances adhesion and produces a similar failure mode. However the potential threats in the manipulation of highly concentrated isocyanate solutions must be considered. Thus, pretreatment the VR rubber surface with CO_2 plasma followed by the application of a PU adhesive solution with a 4 wt% isocyanate is recommended to obtain adequate adhesive joints.

Chapter 15 - In the this part of the work, a mathematical model of thermolysis of worn tires in overheated steam based on the two-dimensional system of equations of interpenetrating continua is proposed. The porosity is assumed constant by virtue of the fact that because of the presence of a metal cord pieces of rubber in general hold their shape in the process of thermolysis, only decreasing somewhat in volume.

At the initial instant of time the overheated steam hitting pieces of worn tires cools down and condenses. Due to the heat of overheating and phase transition the rubber is heated to a temperature above T = 100°C, and the condensation process thereby ends. The stage of evaporation of the condensate ensues. Upon complete evaporation of the condensate the material is heated further to a temperature at which thermal destruction of the rubber begins. It has been found experimentally that destruction of the rubber occurs with the formation at the initial instant of time of the liquid phase (the rubber surface is covered with drops of destruction products), which partly evaporates and partly undergoes secondary destruction with the formation of gaseous products. It has been established that thermal destruction of the rubber begins at T = 280–300°C and ends at T = 450–500°C and proceeds with heat absorption.

Chapter 16 - Rubber is a polymer often called « plastic » widely used in many industrial applications, such as tires and flooring. The properties of these materials are dependent on the chemical structure, for example the concentration of different monomer constituting of copolymer. So a quantitative characterization is crucial. Different techniques such as Infrared spectroscopy, UV-visible spectrophotometry, RMN, GPC are widely used to characterise the rubber. Static secondary mass spectrometry (S-SIMS) and laser ablation Fourier transform ion cyclotron resonance mass spectrometry (LA-FTICRMS) known to be a powerful technique owing to their high molecular specificity and surface sensitivity. However, a drawback is a lack of quantitative information. Silver deposition on thin film polymer allowed the formation and detection of new secondary ions. In particular, in the case of Styrene butadiene rubber (SBR), silver cationized butadiene (at m/z 161/163) and styrene (at m/z 211/213) are detected. By fitting the relative intensity 211/161 versus percentage of styrene, we have obtained a linear relation.

The same experiments have been investigated by (LA-FTICRMS), but no pretreatment are required. In this case we have followed two relative peaks to the butadiene and styrene monomers respectively at *m/z* 54 and 104.

Mass spectrometry not only bring out molecular information but by adjusting experimental conditions show clearly to be able to give quantitative information.

Chapter 17 - The theoretical frameworks to deal with growth and mechanical effects of strain-induced crystals largely depend on the morphological feature. For the precision materials design based on the simulation technique, such frameworks should be quite significant in order to incorporate the effect of strain-induced crystallization. As for vulcanized natural rubber, however, even the basic type of the induced crystals is still unclear. Thus some researchers assume bundles of extended chains as crystallizing entity, while others assume shish-kebab structure consisted of folded-chain lamellae. There have been several studies on the morphology of strain-induced crystals on the basis of wide-angle X-ray diffraction, small-angle X-ray scattering, electron microscopy, and so on. Along with these previous studies, recent studies on the basis of birefringence measurements suggest that the morphological feature may change from the folded-chain to extended-chain crystals depending on the cross-linking density and strain ratio.

Chapter 18 - Butyl rubber (IIR) possesses excellent resistance to air permeability but at the same time suffers from marginal green strength, fair ozone, heat and reversion resistance. Low percentage of ethylene propylene monomer (EPDM) is blended with IIR in the industries in order to overcome or minimize the above properties.

This study aims in analyzing the dispersion morphology of nanoclay upon direct incorporation in IIR and using EPDM for dispersing nanoclay in IIR. The changes in properties of the IIR nanocomposites in presence and absence carbon black were also studied and compared with pure IIR gum compounds and carbon black filled vulcanizates.

Nanoclay is incorporated in EPDM by solution mixing. The obtained EPDM-nanoclay composites were incorporated in IIR gum compound and in presence of carbon black. The nanoclay employed in this study is Cloisite 20A. The structure and properties of the nanocomposites were analysed by curing study, X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), dynamic mechanical thermal analysis (DMTA), mechanical testing, permeability measurements and scanning electron microscopy (SEM). The morphological studies proved partial exfoliation as well as agglomeration of nanoclay platelets in EPDM and further incorporation of EPDM-nanoclay composites in IIR matrix still enhances the exfoliation of nanoclay platelets. Curing study demonstrates faster scorch time, cure time and increase in maximum torque for the nanoclay loaded IIR compound in presence of EPDM compared to pure and IIR-nanoclay compound without EPDM. DMTA results showed improvement in storage modulus and decrease in tan δ value for the nanoclay loaded IIR composites in presence of EPDM. In addition this particular compound shows enhancement in mechanical and gas barrier properties and furthermore in presence of carbon black the properties were drastically improved may be because of dual filler effect. The tensile fractured surface of the same compound observed through SEM shows highly rough and tortuous path may be due to better interaction between the nanoclay and the polymer matrix.

Chapter 19 - The paramagnetic probe method with the use of free radicals of different dimensions (2,2,6,6-tetramethyl-1-piperidinyloxy and 4-benzoate-2,2,6,6-tetramethyl-1-piperidinyloxy) has been employed to study the effect of the isomeric composition of butadiene units in polybutadienes and butadiene–acrylonitrile copolymers on the number and dimensions of ordered structures. The nature of density fluctuations and defective regions, that is, the regions in which the radicals are sorbed, has been ascertained. It has been shown that the ordered regions are composed of stereoregular chain fragments, while defective regions are enriched with butadiene isomers different from those present in prevailing amounts.

Chapter 20 - Apart from the construction of constitutive laws for fixed porosity, another important issue in rubber mechanics is the prediction of cavity growth. In fact, the cavity growth is one of the most important modes of damage evolution in rubber-like materials. In this topic, one can cite the works of Ogden and Roxburgh (1999) and Dorfmann et al. (2002) who proposed the so-called pseudo-elasticity theory, in which the material response is described by different forms of strain-energy density on primary loading and subsequent unloading. This theory was applied to assess the cavitation damage with success in the case of relatively small values of deformation. On the other hand, many studies were focused on inner surface tearing of cavities. A currently accepted criterion is the maximum chain stretch criterion, stating that a rubber chain can be broken only when it is fully extended. A similar criterion is based on the equi-biaxial stress state on inner cavity boundary under hydrostatic tension. In all these criteria, the cavity begins to grow when a strain variable on cavity's inner boundary reaches a critical level. Another group of cavity growth criteria are established on the basis of energy balance. Williams and Scharpery (1965) proposed using Griffith's formulation to model irreversible expansion of a spherical cavity. This concept was extended by Gent and Wang (1991) and Fond et al. (1996). It is to notice that this criterion was only applied to the case of a spherical cavity in neo-Hookean materials.

The compressible laws issued from the homogenization on a Representative Volume Element (RVE) containing a cavity provides us with a micromechanics basis for cavity growth studies. It is therefore easier to consider the cavity growth by combining the compressible constitutive laws with a physically realistic fracture criterion.

Chapter 21 - Natural rubber was first described by Charles-Marie de La Condamine and François Fresneau of France following an expedition to South America in 1735. In 1770, an English chemist, Joseph Priestley, gave rubber its name when he found it could be used to rub out pencil marks.

Natural rubber comes from many tropical and subtropical trees and shrubs which produce latex, a milky fluid consisting of rubber (cis-1, 4-polyisoprene), protein, water, sterol glycosides, resins, ash, and sugars. Polyisoprene is a commonly known and studied elastomer (elastic polymer) from which natural rubber is processed. Elastomers are large chain molecules that can be extended and yet recover their original shape.

In 1839, Charles Goodyear discovered that heating rubber in the presence of sulfur chemically improved and altered its physical properties. This chemical reaction created sulfur bonds which crosslinked elastic polymers in a process called vulcanization, after Vulcan, the Roman God of fire. Once vulcanized, the rubber molecules are permanently tied together, providing the characteristics needed in elastics. The resulting compound has increased tensile strength, resistance to deformation, and wide the range of temperatures where rubber maintains its elasticity.

Chapter 22 - Modification of polychloroprene-based glue compositions with nitrogen- and phosphorus-containing adhesion promoters was considered. Interaction mechanism of polychloroprene with element-containing adhesion promoters was studied. As a result of conducted investigations it was established that the introduction of element-containing adhesion promoters in polychloroprene-based glue compositions in quantities of 0,05-3,0% promotes the substantial durability increasing of glue fastening of various caoutchoucs-based vulcanized rubbers in a 0,5-3,5 times average. Mechanism of interaction of glue with substrate which consists in enhancement of diffusion processes as a result of polychloroprene macromolecule modification was proved. Surface structure of glue films was investigated.

Chapter 23 - Consumers and industrial activities increasingly require goods and services that suit as much as possible to their needs and tastes. The footwear industry has followed these trends leading to the need to use a variety of materials and components that are presently used from casual shoes to technical products such as safety and protective footwear.

Rubber is among these materials and has been strongly used in the production of shoe soles since its discovery in 1837 by Goodyear. Although rubber, more precisely vulcanized rubber, present some drawbacks in comparison with other polymers used in footwear applications (e.g. higher density, longer processing operations and slightly higher costs) it gathers a group of superior physical properties suitable for shoe sole production, namely, durability, abrasion resistance, tensile resistance, tear strength resistance, slip resistance, oil resistance and the ability to be molded in different colors.

This chapter focuses on the properties and physical-mechanical guidelines for vulcanized rubber applications in footwear and on the description of recent developments regarding shoe sole applications. In particular the work carried out in shock absorption properties in vulcanized rubber, natural rubber incorporating mercerized natural fibers of sisal, jute, hemp and bamboo will be presented.

Chapter 24 - The paper describes works related to the development of an improved version of the rubberized footwear as an external orthotic fixed ankle brace (FAB), required for the cured leprosy patients for prevention of deformities, economic rehabilitation and thereby enhancing their self-esteem and social well-being.

Use of glass fibre reinforced polypropylene, as leg piece of FAB containing window cut-outs and narrowing of the medio-laterial diameter enabled to reduce the average weight of the appliance. Ethylene vinyl acetate (EVA) based rubber foam was developed, stripped into sheets of desired thicknesses and used for making the flexible insole and lining components. Filled XLPE material, in place of natural cork, was used as a rocker for lesser water ingress and ease of machining of the item with desired shape and size. Development of the outer rubber sole, rubber coated nylon fabric etc., were carried out using neoprene particularly to impart flame retardency, abrasion and chemical resistances, flexibility and longer service life to the modified FABs. All the components were produced at an infrastructure facility specially developed for the purpose at Bandorawalla Leprosy Hospital under Poona District Leprosy Committee (PDLC), Pune.

CONTENTS

Preface vii

Chapter 1 Reinforcement of Rubber Compounds by Different Fillers: Recent Achievements **1**
S. Ostad Movahed and M. Alimardany

Chapter 2 Mechanical Behavior of Elastomers: Experimental Determination and Numerical Modeling **83**
Dario Amodio, Giacomo Palmieri and Marco Sasso

Chapter 3 Properties and Mechanical Reliability of Elastomers **171**
N. Aït Hocine, S. Méo, F. Lacroix and P. Meroz

Chapter 4 Smart Electric Elastomer Based on Electronic and Ionic Operational Mechanism **211**
X. P. Zhao and L. M. Hao

Chapter 5 Rubber Types, Properties and Uses **267**
Sawsan F. Halim and Maher Z. Elsabee

Chapter 6 Blends of Epoxidized Natural Rubber and Thermoplastics **305**
C. H. Chan, H. W. Kammer, L. H. Sim and M. K. Harun

Chapter 7 Natural Rubber Latex/Chitosan Blends **337**
Vijayalakshmi Rao and Jobish Johns

Chapter 8 Recycled Rubber: Composite Matrix **377**
Cristina Cazan and Anca Duta

Chapter 9 Durability of Rubber during Thermo and Photo-Ageing **399**
David Ruch, Grégory Mertz and Fatima Hassouna

Chapter 10 The Role of Styrene Butadiene Styrene as a Modern Multifunctional Thermoplastic Elastomer **427**
James E. Kennedy

Chapter 11 Deformational Properties of Silica Filled Styrene-Butadiene Rubber under Uniaxial Tension **455**
K. Aniskevich, O. Starkova, J. Jansons and A. Aniskevich

Chapter 12 Uses of Scrap Rubber Tires **477**
Hing-Ho Tsang

Chapter 13 Modeling and Simulation of Nanofilled Crosslinked Rubber Using Coarse-Grained Molecular Dynamics **493**
Hiromasa Yagyu

Chapter 14 Isocyanate Priming of Vulcanized Rubber **509**
M. Mercedes Pastor-Blas and Ana B. Ortíz-Magán

Chapter 15 Steam Thermolysis of Technical Rubber Material **531**
Henadz Zhurauski, Vitali Zhdanok, Nikolai Pavlukevich and Valeri Babenko

Chapter 16 Characterisation of Rubber by Means of Mass Spectrometry **549**
David Ruch and Fatima Hassouna

Chapter 17 Morphology of Strain-Induced Crystals in Vulcanized Natural Rubber **563**
Masatoshi Tosaka

Chapter 18 Effect of EPDM-Nanoclay Composites in Butyl Rubber Gum Compounds and in Presence of Carbon Black Filled Vulcanizates **575**
R. Rajasekar, G. C. Nayak and C. K. Das

Chapter 19 The Structure of Elastomers **591**
N. M. Livanova and S. G. Karpova

Chapter 20 Cavity Growth **601**
Jia Li

Chapter 21 Rubber in Dentistry **611**
Francis K. Mante, Rose O. Wadenya, Sennay Stefanos and Bekir Karabuchack

Chapter 22 Modification of Polychloroprene-Based Glue Compositions with Element- Containing Adhesion Promoters **627**
N. A. Keibal, S. N. Bondarenko, V. F. Kablov and D. A. Provotorova

Chapter 23 Rubber for Footwear Applications **635**
R. M. Silva, J. L. Rodrigues, V. V. Pinto M. J. Ferreira and C. M. Pereira

Chapter 24 Development of Footwear for Leprosy Patients **659**
D. K. Setua

Index **669**