Preface

Natural rubber is a very versatile material that has been successfully used in engineering applications for over a century. As the rubbers in their virgin forms are too weak for practical applications they are mixed with other materials (compounding ingredients) to improve processability and to develop the properties required for various applications. Vulcanization or curing is an essential step in the manufacture of any rubber product. In the vulcanization reaction of rubbers, accelerators perform the important functions of bringing down the time needed for vulcanization, controlling the scorch safety and managing the type and number of cross links formed.

Of the various chemicals used in the rubber industry, some are known to produce nitrosamines. Some of these nitrosamines (by-products of rubber vulcanization) have been classified as potential human carcinogens by the International Agency for Research on Cancer (IARC). Therefore the rubber industry has to take measures for the control of nitrosamines. One of the options for controlling the nitrosamines is using nitrosamine safe formulations in rubber compounding.

Nitrosamines are of particular relevance to the rubber industry as these materials can be formed in rubber articles through the reactions of many of the accelerators used in formulations. The accelerators and sulphur donors that form hazardous nitrosamines (regulated) are tetramethyl thiurammonosulfide (TMTM), tetramethyl thiuramdisulfide (TMTD), N-oxydiethylenedithiocarbamyl N'-oxydiethylenesulfenamide (OTOS) and N-oxydiethylene 2-benzothiazolesulfenamide (MBS). Certain accelerators, because of their specific structure produce safe or non-regulated nitrosamines. Zincdibenzyl dithiocarbamate (ZBEC), tertiarybutyl benzothiazolesulfenamide

(TBBS), Tetrabenzyl thiuramdisulfide (TBzTD) and Dithio dicaprolactam (DTDC) are some of the non-regulated nitrosamine accelerators.

As per German regulations related to the activities involving hazardous substances including their classification and labelling (Technical Rules for Dangerous Substances (TRGS 522)), TBzTD is a non-regulated accelerator and is safe to replace thiurams such as TMTD. Similarly nitrosamine producing accelerators such as MBS can be replaced by non–regulated nitrosamine producing accelerators such as N-cyclohexyl-2-benzothiazole sulfenamide (CBS), N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) and TBBS. In order to study the effect of accelerators on properties of the vulcanizates, it is convenient to select a low sulphur (Efficient Vulcanization (EV)) vulcanization system. For low sulphur vulcanization, thiurams are normally used in combination with sulfenamides as accelerators.

Though the gum natural rubber vulcanizates exhibit good tensile strength, fillers are generally incorporated in commercial rubber compounds for reinforcement, improved processability and cost reduction. The most effective reinforcing filler used in rubber industry is carbon black. One of the non-black reinforcing fillers with reinforcing properties closer to carbon black is precipitated silica. Though the presence of silica in rubber formulations offers high strength, it is accompanied by processing problems such as high viscosity, cure retardation and compound stiffness.

Several modifications of silica filler such as heat treatment, chemical modification of the filler surface groups, grafting of polymers on to the filler surface and use of promoters or coupling agents have been reported to improve the rubber-filler interaction. One of the widely used silane coupling agents is bis(triethoxysilylpropyl) tetrasulfide (TESPT). Epoxidised natural

rubber (ENR) shows polarity and bi-functionality. ENR may be considered as an alternative to silanes.

The present work focuses on the preparation of non-cytotoxic vulcanizates based on natural rubber using safe accelerators.

The thesis consists of eight chapters. A concise introduction to the topic is presented in the first chapter. The second chapter describes the details of materials used and experimental procedures used for the study. Chapter 3 has been divided into two parts. This chapter presents the studies on natural rubber gum vulcanizates based on formulations containing regulated binary accelerator (MBS and TMTD) system. Vulcanizate with comparable properties were prepared by replacing MBS with non-regulated (safe) TBBS and TMTD with non-regulated TBzTD. The use of DCBS and N, N-dibenzyl-2-benzothiazolesulfenamide (DBBS) as non-regulated sulfenamide type accelerators is described in Chapter 4. Chapter 5 is divided into two parts. The chapter describes the evaluation of the effect of carbon black and silica on the cure characteristics, mechanical properties, sorption properties, thermal properties and fluid resistance of nitrosamine-safe natural rubber vulcanizates containing TBBS and TBzTD. Chapter 6 is divided into two parts. This chapter discusses the use of epoxidised natural rubber as a modifier in silica filled natural rubber and comparison of the properties of the vulcanizates with that of silane modified silica filled natural rubber vulcanizate. Analysis and comparison of the effect of heat ageing on the properties of natural rubber vulcanizates prepared using antioxidants N-(1, 3-dimethyl butyl)-N'-pheny1-p-phenylenediamine (6PPD), polymerized 1,2-dihydro-2,2,4-trimethyl quinoline (commercial TQ) and dimer-rich high pure grade TQ (HPG) are described in Chapter 7. The evaluation of cytotoxicity of the vulcanizates for detecting the toxicity of

the soluble substances present in the rubber vulcanizates has been presented in chapters 3-7. The conclusions of the investigations presented in the thesis are given in chapter 8.

Abstract

Conventional accelerators (N-oxydiethylene 2-benzothiazolesulfenamide (MBS) and tetramethyl thiuramdisulfide (TMTD)) used in rubber vulcanization are listed under the category of cancer producing nitrosamine generating (regulated) chemicals. The vulcanizates prepared using these accelerators are not safe. Safe natural rubber (NR) vulcanizates were prepared using non-regulated (safe) accelerators viz. tertiarybutyl benzothiazolesulfenamide (TBBS) and tetrabenzyl thiuramdisulfide (TBzTD) with properties comparable to that prepared using the conventional accelarators. The results of cytotoxicity testing confirmed the safety of the vulcanizates. Safe natural rubber vulcanizates were also prepared using non-regulated accelerators (either N,N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) or N,N-dibenzyl-2-benzothiazolesulfenamide (DBBS)) as a single accelerator and as binary accelerators (in combination with TBzTD). Mechanical properties of these vulcanizates were compared. Effect of carbon black and precipitated silica on the cure characteristics and mechanical properties of the safe NR vulcanizates prepared using safe accelerators (TBBS and TBzTD) were analysed. Silane coupling agent was incorporated in silica-filled natural rubber compounds to reduce the processing difficulties and to improve the rubber-filler interaction. The role of epoxidised natural rubber (ENR) as an economic substitute for silane coupling agent was also examined. Studies include thermo-oxidative ageing, sorption characteristics, scanning electron microscopy and thermogravimetric analysis. The rubber-filler interaction, fluid resistance and cytotoxicity of the vulcanizates too were evaluated. The efficiency of the antioxidants - commercial polymerized 1,2-dihydro-2,2,4–trimethyl

quinoline (TQ), dimer-rich high pure grade TQ (HPG) and N-(1,3-dimethyl butyl)-N'-phenyl-p-phenylenediamine (6PPD) in safe vulcanizates was compared. The cytotoxicity of these vulcanizates was evaluated.

Keywords:

Conventional accelerators, Vulcanization, Nitrosamines, Non-regulated accelerators, Cytotoxicity, Binary accelerators, Carbon black, Precipitated silica, Silane coupling agent, Epoxidised natural rubber, Thermo-oxidative ageing, Sorption characteristics, Scanning electron microscopy, Thermogravimetric analysis, Antioxidants.