DEVELOPMENT OF PROPERTY CORRELATIONS FOR NITROSAMINE SAFE BINARY ACCELERATOR SYSTEMS IN SULFUR VULCANIZED NATURAL RUBBER

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DECLARATION OF CANDIDATE AND SUPERVISORS

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ABSTRACT

In sulfur vulcanization of natural rubber (NR), organic accelerators play an important role by increasing the rate of vulcanization and enhancing the properties of the end products. Most of the traditional accelerators are derivatives of dialkyl amines (tetra alkyl thiuram disulfides, zinc dialkyl dithiocarbamates) and are thus capable of generating regulated nitrosamines, which are also known as carcinogenic in human. Therefore, there is a requirement for alternative accelerators, which can be used as substituents for traditional accelerators. As a result, variety of novel accelerators had been developed in the past in respect to changes to the basic structure of traditional accelerators. Nitrosamine-safe, dibenzyl amine containing thiurams (tetrabenzylthiuram disulfide - TBzTD) and dithiocarbamate (dibenzyl dithiocarbamate - ZBeC), are two commercially available such accelerators. In addition, nitrosamine-free diisopropyl xanthogen polysulfide (DIXP) accelerator is another possible alternative accelerator. Although application of DIXP in NR latex and other synthetic rubbers (bromobutyl elastomers and synthetic polyisoprene latex compounds) has been found, its use as a single accelerator, or in binary accelerator system, for NR compounding has not been found and the available information on use of DIXP in NR is also very scanty. Further, no studies were reported specifically on the use of DIXP combined with other nitrosamine-safe accelerators in efficient sulfur vulcanizing system to produce vulcanizates from dry rubber-based NR. Thus, the present research aims to study the behavior of DIXP as a single accelerator and in combination with TBzTD, ZBeC and N-tert-butyl-2- benzothiazole sulfenamide (TBBS) which is commonly used nitrosamine-safe sulfenamide accelerator to establish nitrosamine-safe binary accelerator system/s for sulfur vulcanized NR to overcome the issues associated with the traditional accelerator/s.

In that context, cure characteristics of NR compounds, physico- mechanical properties of NR vulcanizates accelerated with DIXP, TBzTD and ZBeC were evaluated and compared with compounds/vulcanizates accelerated with TBBS accelerator. Effect of three different combinations of DIXP/TBBS, DIXP/TBzTD and DIXP/ZBeC binary accelerator systems on cure, physico-mechanical, crosslink density, ageing, dynamic mechanical and thermal properties of NR vulcanizates prepared with efficient sulfur vulcanizing system were evaluated and compared with those of the vulcanizates prepared with single accelerators. Correlation between crosslink density and properties of DIXP accelerated vulcanizates were evaluated for the three binary accelerator systems as well as for overall DIXP accelerated vulcanization. Intermediates generated during vulcanization of DIXP-accelerated NR was analyzed by evolved gases using coupled thermogravimetric infrared (TGA-IR) spectroscopy and gas chromatographic-mass spectrometry (GC-MS) and cure kinetics.

Results indicate that in comparison to the vulcanizates prepared with nitrosamine-safe TBBS, TBzTD and ZBeC accelerators, most of the cure properties and physico-mechanical properties of vulcanizates prepared with DIXP accelerator are inferior. Nevertheless, DIXP accelerator provides satisfactory results regarding cure time compared to the TBBS accelerator. However, a significant enhancement in cure and physco-mechanical properties of vulcanizates prepared with the three binary accelerator systems was noticed and vulcanizates accelerated with DIXP/TBBS (0.6/1.4), DIXP/TBzTD (1.4/0.6) and DIXP/ZBeC (1.4/0.6) showed optimum mechanical properties. Further, the trend in the variation of properties of vulcanizates prepared with DIXP accelerated systems against the crosslink density follows the same pattern of variation of traditional accelerators irrespective of the accelerator system used. Finally, a crosslinking reaction mechanism was proposed based on the evidence of the evolved gases, cure kinetics and considering the commonly accepted mechanism of accelerated sulfur vulcanization for elastomers.

Key words: Natural rubber compounds, nitrosamine-safe binary accelerator systems, physico-mechanical properties, dynamic mechanical properties, thermal properties, correlation, crosslinking mechanism

DEDICATION

To my ever-loving parents

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LIST OF ABBREVIATIONS`

Abbreviation	Description
2DLC	Two-Dimensional Liquid Chromatography
A/S	Accelerator to Sulfur
BPTD	Bis (N-Benzyl Piperazino) Thiuram Disulfide
BIIR	Bromobutyl Rubber
BR	Butadiene Rubber
CRI	Cure Rate Index
COS	Carbonyl Sulfide
CS_2	Carbon Disulfide
CBS	N-Cyclohexyl-2-Benzothiazole Sulfenamide
CV	Conventional Sulphur Vulcanizing System
DIXP	Diisopropyl Xanthogen Polysulfide DMTA
	Dynamic Mechanical Thermal Analysis
DIPDIS	Bis (Diisopropy1) Thiophosphoryl Disulfide
DTEP	Dithio bis (N-β-hydroxy Ethyl Piperazine)
EPTD	Bis (N-Ethyl Piperazine) Thiuram Disulfide
EV	Efficient Sulphur Vulcanizing Sytem
FTIR	Fourier Transform Infrared
FLD	Fluorescence Detectors
GC	Gas Chromatography
GC-MS	GC-Mass Spectrometry
GC-FID	GC-Flame Ionization Detectors
GC-NCD	GC-Chemiluminescence Detectors
GC-TEA	GC-Thermal Energy Analyzer 4
GC-NPD	GC-Nitrogen Phosphorus Detectors
GRT	Ground Rubber Tyre
Hdmtc	Dimethyl Dithiocarbamic Acid

HPLC	High Performance Liquid Chromatography
IARC	International Agency for Research on Cancer
IPA	Isopropyl Alcohol
IL	Ionic Liquid
LC	Liquid Chromatography
MBS	2-(4-Morpholinothio)-Benzothiazole
MBT	2-Mercapto Benzothiazole
MS	Mass Spectrometry
NDMA	N-Nitroso Dimethyl Amine
NR	Natural Rubber
NDMA	N-nitroso Dimethyl Amine
NDEA	N-nitroso Diethyl Amine
NMOR	N-nitroso Morpholine
NDBzA	N-Nitroso Dibenzyl Amine
NRPRA	Natural Rubber Producers Research Association
NOCs	N-Nitroso Compounds
NDPhA	N-Nitroso Diphenyl Amine
NDELA	N-Nitroso Diethanol Amine
NDBA	N-Nitroso di-N-Butylamine
NIOSH	National Institute for Occupational Safety and Health
NPIP	N-Nitroso Piperidine
NIST MS	National Institute of Standards and Technology Mass Spectral
PR	Photochemical Reactor
PPTD	Bis (N-Phenyl Piperazine) Thiuram Disulfide
SIM	Selective Ion Monitoring
SEV	Semi Efficient Sulphur Vulcanizing System
RPA	Rubber Process Analyzer SBR
	Styrene-Butadiene Rubber
TMTD	Tetramethyl Thiuram Disulfide
TBzTD	Tetrabenzyl Thiuram Disulfide
TME	2,3-Dimethyl-2-Butene

TMTP	Tetramethyl Thiuram Polysulfide
TGA	Thermogravimetric Analysis
UV	Ultra Violet
UHPLC	Ultrahigh-Performance Liquid Chromatography
ZDEC	Zinc Diethyl Dithiocarbamate
ZBeC	Zinc Dibenzyl Dithiocarbamate
ZDMC	Zinc Dimethyl Dithiocarbamate
ZDNC	Zinc Diisononyl Dithiocarbamate
ZnO	Zinc Oxide
ZDAC	Zinc Dialkyl Dithiocarbamate
ZPDC	Zinc (N-Methylpiperazino) Dithiocarbamate
ZBPDC	Zinc (N-Benzyl Piperazino) Dithiocarbamate
ZEPDC	Zinc (N-Ethyl Piperazino) Dithiocarbamate
ZPPDC	Zinc (N-Phenyl Piperazino) Dithiocarbamate
ZDBC	Zinc Dibutyl Dithiocarbamate