POLYSULFIDE OLIGOMER SEALANTS

SYNTHESIS, PROPERTIES, AND APPLICATIONS

Yuri N. Khakimullin, DSc
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ABOUT THE AUTHORS

Yuri N. Khakimullin, DSc

Yuri N. Khakimullin, DSc, is a Professor in the Department of Chemistry and Processing Technology of Elastomers at Kazan National Research Technological University in Kazan, Russia. He has written four monographs, has written over 150 articles published in scientific journals, and holds 31 patents. His research areas include the synthesis, technology and processing of rubber and sealants based on polysulfide oligomers and elastomers and processes of radiation degradation of polymers..

Vladimir S. Minkin, DSc

Vladimir S. Minkin, DSc, is a Professor in the Physics Department at Kazan National Research Technological University in Kazan, Russia. He is the author of four monographs, over 200 articles, and 12 patents. He has authored four monographs, written over 200 scientific articles, and holds 12 patents. His research interests include NMR in reactive oligomers; investigation of the structure and properties of sulfur-containing composite materials based on liquid thiokols; application methods of magnetic spectroscopy to study the structure, phase composition, molecular mobility of petroleum and petroleum products, and natural bitumen; and the development of new devices for rapid analysis and group composition heavy oil and natural bitumen.

Timur R. Deberdeev, DSc

Timur Deberdeev, DSc, is a Professsor in the Department of Processing Technology of Polymers and Composite Materials at Kazan National Research Technological University in Kazan, Russia. He is the author of two monographs, has written over 60 scientific papers, and holds 13 patents. His research areas include the synthesis, technology, and processing of rubber and polymers, PVC, and composite materials based on epoxyamine systems.

LIST OF ABBREVIATIONS

1;1-NT; 2; 2-NT	liquid thiokol grades
7-1; 7-20; TMGPh-11; TGM-3; MGPh-9	grade of oligoesteracrylates
Agidol AF-2	catalyst, a Mannich base Transamination Product
AM-05, AM-05K	Grades of Thiokol Sealants, Used in Construction Industry
BN70/30	Petroleum Bitumen Grade
CED	Cohesion Energy Density
DDE	Disulfide-Disulfide Exchange
DG-100	Channel Type Carbon Black Grade
DTA	Differential-Thermal Analysis
DTB	Density of Transversal Bonds
FTD	Functional Type Distribution parameters
HP-30; HP-470; HP-52	Grades of Chloroparaffines
IPN	Interpenetrating Polymer Network
LT-1; LT-1K; SG-1; SG-1K	Grades of TPM-2-Based Sealants, Used in Construction Industry
MB	Mannich Bases
MNI ITEP	Moscow State and Design Institute of Typology and Experimental Design
MTD-2	Natural Chalk Grade
MWD	Molecular Weight Distribution
NVB-2	Liquid Thiokol Grade
OEDGA-50	Oligoester based on Ethyleneglycol and Diethyleneglycol (1:1) Mixture and Adipinic Acid
OM-3	Mannich Base
P-803; PM-50; PM-70	Furnace Type Carbon Black Grades
PIC	Polyisocyanate
PN-1; PN-9119	Grades of Unsaturated Polyesters
PSO	Polysulfide Oligomer Sealants
SFA	Synthetic Fatty Acids
SKUDF-2, FP-65	Oligobutadienediol-Based Prepolymers with Isocyanate End Groups

SKUFE-4	Polyester-Based Prepolymers with Isocyanate End Groups
SKUPFL-100	Oligooxymethyleneglycol-Based Prepolymer with Isocyanate End Groups and Molecular Weight of 1000
SKUPPL-4503;	Oligo Oxypropyleneglycol-Based Prepolymers
SKUPPL-5003	with Isocyanate End Groups and Molecular Weight of 4503 and 5003 Correspondingly
Solid thiokol "DA"	Solid Thiokol Grade
STIZ-30	Thiokol Sealant
Thiuram D	Tetramethylthiuramdisulfide
TMA	Thermomechanical Analysis
TMD	Transversal Magnetization Decay
TPE	Thiol-Polysulfide Exchange
TPM-2	Thiol-Containing Polyester with End SH-Groups
U-30M; U-30MES-5; U-30MES-10; UT-31; UT-32; UT-34; 51UT-36; 51UT-37; 51UT-38; VIT	Grades of Thiokol Sealants
U30 E-10; U30 E- 5	Grades of Sealing Pastes
USPE	unsaturated polyesters
E-40, ED-20	Epoxy Diane Resin Grades

LIST OF SYMBOLS

ξ	adhesion parameter
ν_{chem}	chemical density of transversal bonds
ν_{eff}	effective chain density
δp	solubility parameter
k_e	rate constant
$\lg\eta$	dependence of viscosity
$\lg\gamma$	shear rate
H_2^2	second moment values
$[MnO_2]cryst$	manganese oxide crystallite
R'	alkylene
R'_{in}	radical products of Mannich base decay
R_{in}^*	radicals
$T_{21}(t)$	induction period
T_{2final}	final relaxation times
T_{flow}	viscous-flow transition temperature
T_{glass}	glass-transition temperature
T_{soft}	softening temperature
$\bar{f}_n$	number-average functionality
γ	shear rate
ε_{rel}	relative elongation

ABSTRACT

This book deals with problems of synthesis, vulcanization, modification, and the study of structure and properties of highly filled sealants based on polysulfide oligomers.

The book summarizes data on chemistry and synthesis technology of liquid thiokols and thiol-containing polyesters, and their structure and properties. It provides scientific information on chemistry and mechanisms of liquid thiokols vulcanization by oxidants and in polyaddition reaction. Basic formulation principles for sealing compositions are given; their properties and application range are described.

The monograph provides the results of authors' research on vulcanization and modification of thiokol sealants, using thiokol-epoxy resin copolymers, unsaturated polyesters and isocyanate prepolymers of a various nature. It combines research on vulcanization mechanisms of polysulfide oligomers by manganese dioxide, sodium bichromate and zinc oxide, as well as on the structure and properties of sealants, based on liquid thiokol and TPM-2 polymer, depending on the nature and ratio of used oligomers. This publication also gives information on the influence of fillers on vulcanization kinetics, rheological and physical-mechanical properties of sealants, depending on the nature of PSO.

The book is meant for scientific and engineering personnel at institutes, science centers and companies pursuing research in design, structure and properties of reactive oligomers and related compositions and dealing with their production and application, as well as for professors, postgraduates and graduate students in the field of chemical technology education.

PREFACE

Polysulfide oligomers are reactive low-molecular rubbers and the representatives of the earliest feedstock for industrial production of cold cure sealants in the world. The main reason of such sealants being widely used in modern construction, mechanical engineering and aircraft industries relates to their unique range of properties and corresponding excellent performance. This range combines outstanding gas impermeability and atmosphere resistance with oil and gasoline resistance. In addition, high demand for polysulfide oligomers roots in their effective curing ability via oxidation of end SH-groups as well as in their high reactivity to various functional groups, such as epoxy, acrylate and isocyanate ones. It is the basis for effective chemical modification of sealants and control of product composition and related properties of at the stage of sealing blend preparation. On the other hand, sealants are commercially attractive because of their high stability during pre-application storing. All the aforesaid proves the technology of curing via end SH-groups to be extremely attractive and perspective.

This monograph is dedicated to aspects of synthesis, properties and application of polysulfide oligomer sealants. First two chapters provide a survey of existing technologies for synthesis of liquid thiokols and oligomers with end SH-groups (mainly using oligooxypropyleneglycols and thiol-containing polyesters) as well as curing methods, composition and application of polysulfide oligomer sealants. These chapters also provide systematized up-to-date information, available in literature after Lucke's monograph (Lucke H. Aliphatic Polysulfides. Monograph of an elastomer) publications by Huthig and Wepf in 1994. Next chapters summarize research results of monograph authors in curing, chemical modification and filling of sealants, based on liquid thiokol and TPM-2 polymer, as well as the study of their structure and performance (including service properties characterization) at a high filling rate.

The book may be useful for researchers with area of interest covering synthesis and application of polysulfide oligomers as well as for various scientists and engineers engaged in synthesis, modification and processing of reactive oligomers.

Prof. Gennady E. Zaikov, Editor
Head of Polymer Division,
N.M. Emanuel Institute of Biochemical Physics,
Russian Academy of Sciences

INTRODUCTION

There is a stably growing modern tendency of consumption polymer composites designed for outdoor application. Composite materials containing unsaturated elastomers and oligomers are the most popular components for sealing and waterproofing materials as they demonstrate durable and effective resistance to such aggressive factors as ultraviolet radiation, ozone and water in a broad temperature range of –60 to +100°C.

Sealing materials based on reactive oligomers become more and more important today. Polysulfide oligomer sealants (PSOs), with thiokol as the main representative, occupy a special place among these materials. However, their application in Russia was limited to special purposes until the 1980s. These products used to take only 10% of construction, market, while produced thiokol sealants were low-filled.

The consumption pattern of thiokol sealants is quite different today, as they have become highly demanded for sealing interpanel seams and especially for sealing glass packets. Therefore, considering the growing world deficit of liquid thiokols, there is a necessity of application of highly filled PSO-based compositions. The scientific basis for vulcanization and modification of thiokol sealants has been mainly developed in studies of N. P Apuhtina, R. A. Shljahter, L. A. Averko-Antonovich, P. A. Kirpichnikov, R. A. Smyslova, E. M. Fettes, S. Iorzhak Dzh, M. Berenbaum, E. Dahsel't, T. S. P. Li, G. Ljuke et al. However, development of highly filled sealants based on liquid thiokol or thiol-containing polyester–TPM-2 polymer has revealed almost total deficiency of research on the influence of inert fillers on their vulcanization process and physical-mechanical and service properties. It should be noted that research, which acquires a special interest today, concerns introduction of more available reactive oligomers and oligomers of another nature into thiokol-based sealing formulations, and the study kinetic behavior of vulcanization network formation processes, modification and vulcanization mechanisms. The results of aforementioned research provide a scientific ground for modification and vulcanization processes, the structure of forming vulcanization networks, and the properties of PSO-based sealants in the highly filled state.

This book is a logical continuation of earlier publications by Professor L. A. Averko-Antonovich, with coauthors [1], Professor V. S. Minkin [2] and the authors [3]. In view of the aforesaid and considering the fact of the absence of recent summarizing publications in this area, this monograph provides data on the chemistry and technology of PSO production, on vulcanization, modification and application of related sealants, as well as the results of research, pursued by the authors themselves.

KEYWORDS

- **chemistry and synthesis technology**
- **cold cure sealants**
- **industrial production**
- **liquid thiokols and thiol-containing polyesters**
- **oligomers**
- **polysulfide**
- **reactive low-molecular rubbers**

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CONTENTS

CHAPTER 1

SYNTHESIS, STRUCTURE AND PROPERTIES OF POLYSULFIDE OLIGOMERS

CONTENTS

1.1 CHEMISTRY AND PRODUCTION TECHNOLOGY OF POLYSULFIDE OLIGOMERS

Aliphatic polysulfides (or thiokols) are oligomers having fragments with disulfide bond and containing two or more mercaptan groups: HS – R $(SS–R')_n$ – SH. The term "Thiokol" originates in the trademark of polysulfide oligomers produced by the "Thiokol Chemical Corp." (USA) (later known as "Morton Inter. Inc.") [1].

Polysulfide oligomers (PSO) are reactive oligomeric compounds forming, if cured, sealants with a unique range of properties. High thermodynamic flexibility and the presence of chemically bound sulfur in the main chain of such compounds provide the respective sealants with a high fuel resistance, gas-tightness, water resistance as well as increased resistance to ultraviolet, solar radiation and ozone thanks to the main chain's saturation. PSO-based sealants have the ability of noncontractive low-temperature curing and are also highly durable. Acetal groups, on the other hand, favor acidic and basic molecular hydrolysis, but the small additives of a branching agent, introduced during a synthesis of oligomer, increase resistance of PSO vulcanizate to aggressive media both at normal and increased temperatures.

The first commercial production of liquid Thiokol based on 2, 2¢-dichlorodiethylformal with a common name "LP" (LP-2 × LP-3) was deployed in the USA by Thiokol Chemical Corp. in 1943 involving the technology proposed by Patrick and Fergusson [1]. Sodium disulfide was used there as a representative of sodium polysulfide. The production of liquid Thiokol of sodium tetra sulfide was deployed in USSR in 1959. The technology worked out by professor Apouhtina and colleagues was used there [9, 10].

Liquid thiokols are made today of high-molecular polysulfide through their reductive decomposition [9, 10]. Therefore, their production cycle consists of two main stages: the synthesis of a high molecular weight polysulfide and its further ditri or tetrasulfide bond decomposition, resulting in the reduction of a molecular weight (MW) of the produced super polymer (usually down to M_p » 1000,7000).

The synthesis of liquid Thiokol is based on the polycondensation reaction of di- or tri halogen derivatives of organic compounds with sodium di- or tetrasulfide.

The most widespread monomer is 2, 2¢-dichlorodiethyl formal, which provides the highest thermodynamic flexibility for macromolecular chains [2, 11]. 2, 2¢-dichlorodiethyl formal is industrially produced by the acid-catalyzed interaction of ethylene chlorohydrine with formaldehyde in the presence of such compounds as dichloroethane, which are able to extract water zoetrope out of the reaction zone.

$$2\,HOCH_2CH_2Cl + CH_2O \longrightarrow ClCH_2CH_2OCH_2OCH_2CH_2Cl + H_2O$$

There is also an opportunity of the direct 2, 2¢-dichlorodiethylformal syntheses of ethylene oxide, hydrogen chloride and formaldehyde [1, 12].

The method of industrial production of sodium polysulfide is the interaction of caustic soda (40%) with sulfur.

$$6\,NaOH + (2n+1)S \longrightarrow 2\,Na_2S_n + Na_2SO_3 + 3\,H_2O$$

The synthesis is carried out in a vertical agitated reactor at the temperature of 90–95°C. Sodium sulfite, formed during the reaction, interacts with sulfur and forms sodium thiosulfite. Sodium thiosulfate is a byproduct, which is removed in a wastewater during the synthesis. Another way to obtain sodium polysulfide is the reaction involving sodium sulfide:

$$Na_2S + (n-1)S \longrightarrow Na_2S_n$$

The reaction also takes place in water at the temperature of 90–95°C, but byproducts are not formed in this case.

The second method is more preferable due to reduced amount of forming waste. In is up to a producer to choose the method of sodium polysulfide synthesis, taking raw materials availability and economy into account.

Introduction of 0.1÷2.0% mol. of three-functional-1,2,3-trichloropropene (TCP) together with bifunctional monomers gives an opportunity to synthesize branched oligomers, whose vulcanizates are not subjected to a distinct cold-temperature flow and possess better physico-mechanical characteristics, than vulcanizates of linear oligomers.

The majorities of industrial-grade liquid thiokols have a weakly branched structure and contain HS end groups.