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Sreekumar Pisharath

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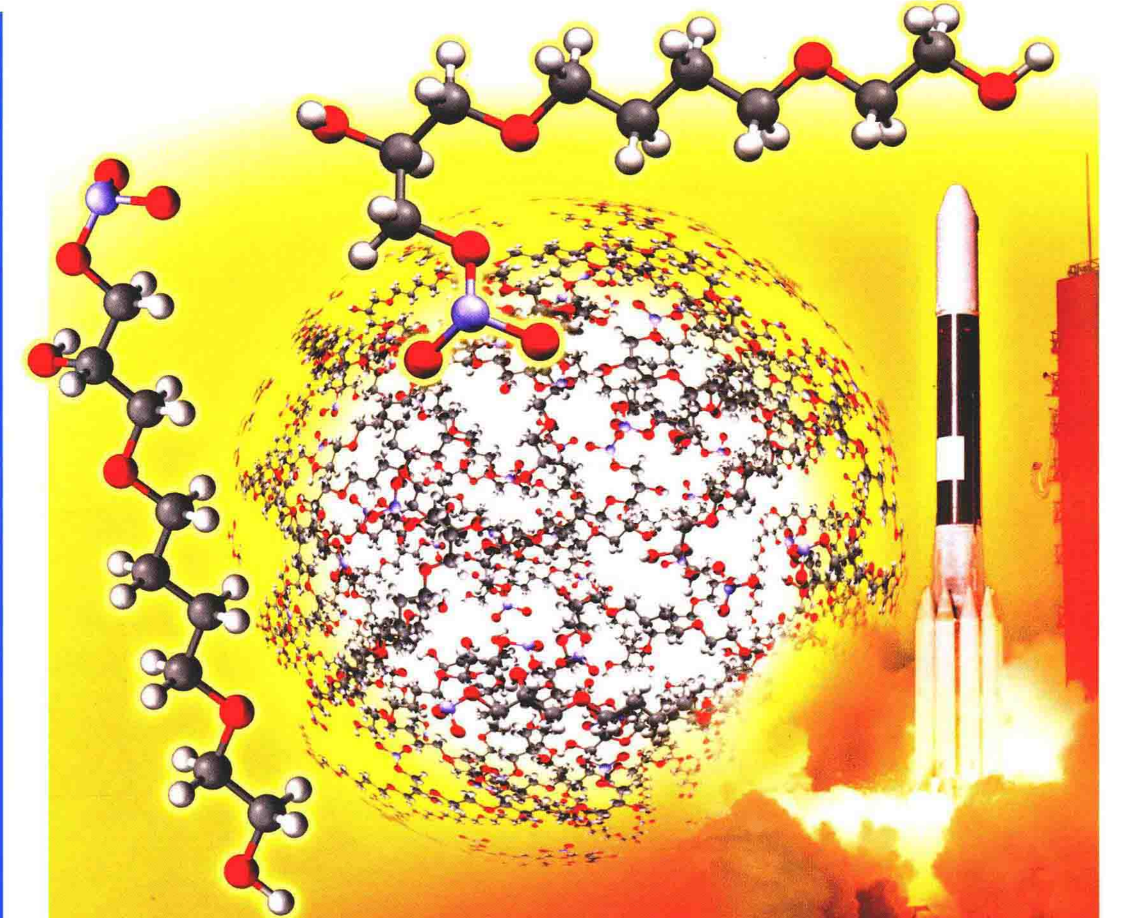
Binders and Plasticizers for Enhancing Performance



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WILEY-VCH Verlag GmbH & Co. KGaA

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Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-33155-0
Typesetting MPS Limited, a Macmillan Company, Chennai, India
Printing and Binding Markono Print Media Pte Ltd, Singapore
Cover Design Formgeber, Eppelheim

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Preface

Over the years, a variety of polymer binders have been developed and used in energetic material composite applications to cope with the global demand for insensitive and high performance propellant and explosive formulations. One of the important milestones in this effort was the development of polymers containing energetic groups, namely azido or nitro groups that release significant amounts of energy under the application of a thermal stimulus. Such type of polymers are referred as energetic polymers. Energetic polymers, when used as binders, provide additional energy and insensitivity to formulations as compared with their inert counterparts. Low molecular weight energetic polymers, with the advantages of a lower migration tendency and less sensitivity to external stimuli, are finding application as energetic plasticizers. Through the years, a range of energetic polymers have been developed as prospective candidates for application as binders and plasticizers. Some of them, namely GAP, Poly(NIMMO), and Poly (GLYN), have reached the stages of mass production.

This book is intended to provide a state-of-the-art overview of the various energetic polymers employed for propellant and explosive formulations. The book is divided into seven chapters. The first chapter details the historical development of the emergence of polymers, including that of the energetic ones, as a vital component in energetic material composites. Chapters 2 and 3 discuss the two important members of the energetic polymer family; the high nitrogen containing polymers and nitropolymers. For the former, the high nitrogen content (in the form of azido and tetrazole groups) provides the polymers with high positive heat of formation and superior energetic properties, albeit resulting in fuel-rich formulations. However, for the latter, the presence of nitro groups offers a better balance of oxygen content and energetic properties. The majority of the commercialized energetic polymers for binder and plasticizer applications belong to these two families. Comparisons are provided wherever possible with the inert binder formulations, to stress the capability of energetic binder formulations for enhancing performance and insensitivity.

Energetic thermoplastic elastomers (ETPEs) have evinced an immense interest due to their unique mechanical and thermal behavior. They are copolymers of energetic polymers that are discussed in Chapters 2 and 3. ETPEs provided a paradigm shift in the processing of energetic material formulations by replacing

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the cast curing process with an environment friendly melt casting process. Chapter 4 presents the various ETPEs used as binders and their application in propellant and explosive formulations.

The application of fluoropolymers as binders is discussed in Chapter 5. Fluoropolymers owe their reactivity to the high electronegativity and oxidizing nature of fluorine. Higher combustion energies could be obtained from composites of fluoropolymers with nanoparticles of combusting metal fuels, such as magnesium and aluminum. This possibility has opened up a new area of energetic materials research called reactive nanomaterials.

Plasticizers derived from energetic polymers with nitro and azido substituents have lower migration tendency as compared with the nitrate ester based energetic plasticizers used in explosive and propellant formulations. The preparation, physical properties, and energetics of azido/nitro polymer based energetic plasticizers are discussed in Chapter 6.

The macroscopic behavior of energetic material composites is the result of the complicated physical processes and microstructure occurring in the composite at multiple length and time scales. Therefore, a multiscale simulation approach is necessary for the prediction of macroscopic properties of energetic material composites from fundamental molecular processes. Simulation of such systems requires theoretical models that range from those including atomistic effects to macroscopic continuum models and passing through the intermediate mesoscopic simulations. Chapter 7 introduces the concept of multiscale modeling in energetic composites and application to simulate the physical and chemical processes in the energetic composites. We hope that the energetic polymers and formulations presented here will be useful in enhancing the search for new high performance and insensitive energetic material composites.

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Abbreviations

A	Frequency Factor
AA	Acrylic acid
ABL	Allegheny Ballistics Laboratory
AC	Acrolyl chloride
ACE	Activated Chain End
ADN	Ammonium dinitramide
ADDF	2,2-Dinitro-1,3-propanediol diformate
AFM	Atomic Force Microscopy
AFEM	Atomic-Scale Finite-Element Method
AIAA	American Institute of Aeronautics and Astronautics
AMM	Activated Monomer Mechanism
AMMO	3-Azidomethyl 3-methyl oxetane
AN	Ammonium nitrate
AP	Ammonium perchlorate
ARC	Adiabatic Reaction Calorimetry
ARL	Army Research Laboratory, USA
ASME	American Society of Mechanical Engineers
AWE	Atomic Weapons Establishment, UK
BABAMP	Bis(azido acetoxy) bis(azido methyl) propane
BAMO	3,3-Bis(azidomethyl) oxetane
BBrMO	3,3-Bis(bromomethyl) oxetane
BCMO	3,3-Bis(chloromethyl) oxetane
BDO	1,4-Butanediol
BDNPA	Bis(2,2-dinitropropyl) acetal
BDNPF	Bis(2,2-dinitropropyl) formal
BDNPA/F	Bis(2,2-dinitropropyl) acetal/formal
BE	Boundary Element
BTTN	1,2,4-Butanetriol trinitrate
BTATz	3,6-Bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine
Bu-NENA	Butyl-*N*-(2-nitratoethylnitramine
B3LYP	Becke 3-Parameter (Exchange) Lee Yang Parr
CAB	Cellulose acetate butyrate
CAL	Calorie

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CC	Copper chromite
CD	Cyclodextrin
CDN	Nitrated cyclodextrin
CEP	Tris(β-chloroethyl) phosphate
CFC	Chlorofluorocarbon
CG	Coarse Grain
CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW)
ClMMO	3-Chloromethyl-3-methyl oxetane
CMDB	Composite Modified Double Base
Comp. B	Explosive composition based on RDX and TNT
COMPASS	Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies
CPX-413	UK's extremely insensitive explosive composition based on NTO, HMX, and Poly(NIMMO).
CRP	Controlled Radical Polymerization
CTPB	Carboxy terminated polybutadiene
CTFE	Chlorotrifluoroethylene
DAAF	4,4-Diamino-3,3-azoxyfurazan
DB	Double Base
DBTDL	Dibutyltin dilaurate
DBP	Dibutyl phthalate
p-DCC	*p*-Bis (α,α-dimethylchloromethyl) benzene
DDM	4,4′-Diaminodiphenylmethane
DEGBAA	Diethylene glycol bis-azido acetate
DEGDN	Diethylene glycol dinitrate
DHT	3,6-Dihydrazino-s-tetrazine
DMA	Dynamic Mechanical Analysis
DMSO	Dimethyl sulfoxide
DMF	Dimethyl formamide
DNAN	2,4-Dinitroanisole
DPD	Dissipative Particle Dynamics
DOS	Dioctyl sebacate
DREV	Defense Research Establishment Valcartier, Canada
DSC	Differential Scanning Calorimetry
DSTO	Defence Science and Technology Organization
DTA	Differential Thermal Analysis
DTG	Derivative Thermogravimetric Analysis
DTIC	Defense Technical Information Center
DRA	Defense Research Agency, UK
E_A	Activation energy
ECH	Epichlorohydrin
EGBAA	Ethylene glycol bis-azido acetate
EGDN	Ethylene glyclol dinitrate
EIDS	Extremely Insensitive Detonating Substance

EOS	Equation of State
ETPE	Energetic Thermoplastic Elastomer
Et-NENA	Ethyl-*N*-nitratoethylnitramine
ESD	Electrostatic Discharge
ESA	European Space Agency
ESR	Electron Spin Resonance
ESTANE	Thermoplastic elastomer based on segmented polyurethane
FOI	Swedish Defence Research Agency
F of I	Figure of Insensitivity
FOX-7	1,1-Diamino-2,2-dinitroethylene
FK-800	A fluorocopolymer developed by 3M having equivalent composition to that of Kel-F800
FTIR	Fourier Transform Infrared
GA	Glycidyl azide
GAP	Glycidyl azide polymer
GAPA	Azido terminated GAP
GC	Gas Chromatography
GLyN (GN)	Glycidyl nitrate
GPC	Gel Permeation Chromatograph
GZT	Guanidine-5,5′-azotetrazolate
H-6	Underwater explosive composition developed by Australia
HDPE	High Density Polyethylene
HFP	Hexafluoropropylene
HFC	Heat Flow Calorimetry
HMMO	3-Hydroxy methyl-3-methyl oxetane
H_{12}MDI	4,4′-Dicyclohexyl methyl diisocyanate (4,4′-diphenylmethane diisocyanate)
HMX	High Melting Explosive or Her Majesty's Explosive
HNF	Hydrazinium nitroformate
HOMO	Highest Occupied Molecular Orbital
HTPB	Hydroxy Terminated Polybutadiene
HYFLON	Fully fluorinated semicrystalline copolymer of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoro-methoxy-1,3-dioxide (TTD)
ICE	Isentropic Compression Experiment
ICI	Imperial Chemical Industries
ICT	Fraunhofer Institut Chemische Technologie, Germany
IM	Insensitive Munition
IMEMTS	Insensitive Munitions and Energetic Materials Technical Symposium
IPDI	Isophorone diisocyanate
I_{sp}	Specific Impulse
IDP	Isodecyl pelargonate
J	Joule
JANNAF	Joint Army–Navy–NASA–Air Force
JA2	Nitrocellulose based propellant

JAX	JA2 propellant loaded with RDX
K	Kelvin
K-10	A mixture of 2-nitroethylbenzene and 2,4,6-trinitroethylbenzene
Kel-F800	Copolymer of vinylidene and hexafluoropropylene
Kraton	Copolymer of styrene and ethylene/butylenes
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
LLM-105	2,6-Diamino-3,5-dinitropyrazine-1-oxide
LOVA	Low Vulnerability Ammunition
LUMO	Lowest Unoccupied Molecular Orbital
LX	Series of explosive formulations developed by LLNL based on fluoropolymer binders
MAPO	Tris(1-(2-methylaziridinyl) phosphine oxide)
MCHI	Methylene bis(cyclohexyl isocyanate)
MD	Molecular Dynamics
MHMO	3-Methyl 3-hydroxymethyl oxetane
MIL-STD	Military Standard
MMA	Methyl methacrylate
M_c	Average molecular weight between crosslinks
M_n	Number average molecular weight
M_w	Weight average molecular weight
Me-NENA	Methyl-*N*-(2-nitroxyethyl) nitramine
MODPOT	*Ab initio* Core Model Potential
MOVO	Molybednum/vanadium oxide catalysts
MRD-CI	Multiple Reference Double Excitation–Configuration Interaction
MS	Mass Spectroscopy
MSIAC	Munitions Safety Information Analysis Center
MTH	Mathematical Theory of Homogenization
MTMO	3-Methyl-3′-(tosyloxymethyl) oxetane
NASA	National Aeronautic Space Agency
NATO	North Atlantic Treaty Organization
NC	Nitrocellulose
NCO	Isocyanate
NDIA	National Defence Industrial Association
NENA	*N*-(2-nitroxyethyl) nitramine (nitratoethylnitramine)
NG	Nitroglycerin
NHTPB	Nitrated hydroxy terminated polybutadiene
NIMMO	3-Nitratomethyl 3-methyl oxetane
NIMIC	NATO Insensitive Munitions Information Center, USA
NMR	Nuclear Magnetic Resonance
NSWC	Naval Surface Warfare Centre
NTO	3-Nitro-1,2,4-triazole-5-one
OB	Oxygen Balance
ODTX	One Dimensional Time to Explosion
OM	Optical Microscopy

ONR	Office of Naval Research
P1	1,3-Bis(azidoacetoxy)-2-azidoacetoxymethyl-2-ethylpropane
PEAA	1,3-Bis(azidoacetoxy)-2,2-bis(azidomethyl) propane
PAN	Polyacrylonitrile
PAX	Picatinny Arsenal Explosive
PB	Polybutadiene
PBA	Poly(butylene adipate)
PBAA	Poly(butadiene–acrylic acid)
PBAN	Poly(butadiene–acrylic acid–acrylonitrile)
PBX	Polymer Bonded Explosive
PBXW-115	PBX developed in USA for underwater applications
PBXN	PBXs developed by US Navy
P_{CJ}	Chapman–Jouguet Pressure
PCTFE	Polychlorotrifluoroethylene
PDMS	Poly(dimethyl siloxane)
PECH	Poly(epichlorohydrin)
PEG	Polyethylene glycol
PETKAA	Pentaerythritol tetrakis (azidoacetate)
PMMA	Poly(methyl methacrylate)
PMVT	Poly(2-methyl-5-vinyl tetrazole)
PNC	Polymer Nanocomposite
Poly(AMMO)	Poly(3-azidomethyl 3-methyloxetane)
Poly(BAMO)	Poly(3,3-bis(azidomethyl) oxetane)
Poly(BEMO)	Poly(bis(ethoxymethyl) oxetane)
Poly(CDN)	Nitrated cyclodextrin polymers
Poly(GlyN) or PGN	Poly(glycidyl nitrate)
Poly(NiMMO)	Poly(3-nitratomethyl 3-methyl oxetane)
Pr-NENA	Propyl-*N*-(2-nitroxyethyl) nitramine
Pe-NENA	Pentyl-*N*-(2-nitroxyethyl) nitramine
PS	Poly(styrene)
PTC	Phase Transfer Catalyst
PTFE	Poly(tetrafluoroethylene)
PU	Polyurethane
PVT	Poly(vinyl tetrazole)
PVDF	Poly(vinylidene difluoride)
QM	Quantum Mechanics
QRX077	Explosive formulation containing HMX, FOX-7, and inert binder
RDX	Research Department Explosive
RVE	Representative Volume Element
SBAT	Simulated Bulk Auto-Ignition Temperature
SEM	Scanning Electron Micrograph
SMATCH	Simultaneous Mass and Temperature Change
SNPE	Societe Nationale des Poudres et Explosifs, France
T	Absolute Temperature

T_g	Glass Transition Temperature
T_m	Melting Temperature
TAAMP	Tris(azido acetoxy methyl) propane
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TDI	Toluene diisocyanate
TEGDN	Triethylene glycol dinitrate
TEX	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane
TFE	Tetrafluoroethylene
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TMETN	1,1,1-Trimethylol ethane trinitrate
TMNTA	Trimethylol nitromethane tris(azido acetate)
TMP	Trimethylol propane
TNT	Trinitrotoluene
TNAZ	1,3,3-Trinitroazetidine
TPB	Triphenyl bismuth
TPE	Thermoplastic Elastomer
TR	Technical Report
TTD	2,2,4-Trifluoro-5-trifluoro-methoxy-1,3-dioxide
UK	United Kingdom
USA	United States of America
VDF	Vinylidene difluoride
Viton	Copolymer of vinylidene fluoride and hexafluoropropylene
VISAR	Velocity Interferometer System for Any Reflector
VOD	Velocity of Detonation
VTS	Vacuum Thermal Stability

Contents

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