Ligand-Regulated Dynamic Ionic–Coordination Networks in Epoxidized Natural Rubber for Self-Healing, Reprocessable, and Mechanically Recoverable Carbon Black–Reinforced Elastomers

Piyawadee Luangchuang[1,2], Vitoon Uthaisangsuk[3], Patcharapit Promoppatum[3], Charoen Nakason[4], Frank Clemens[2], Yeampon Nakaramontri[1]

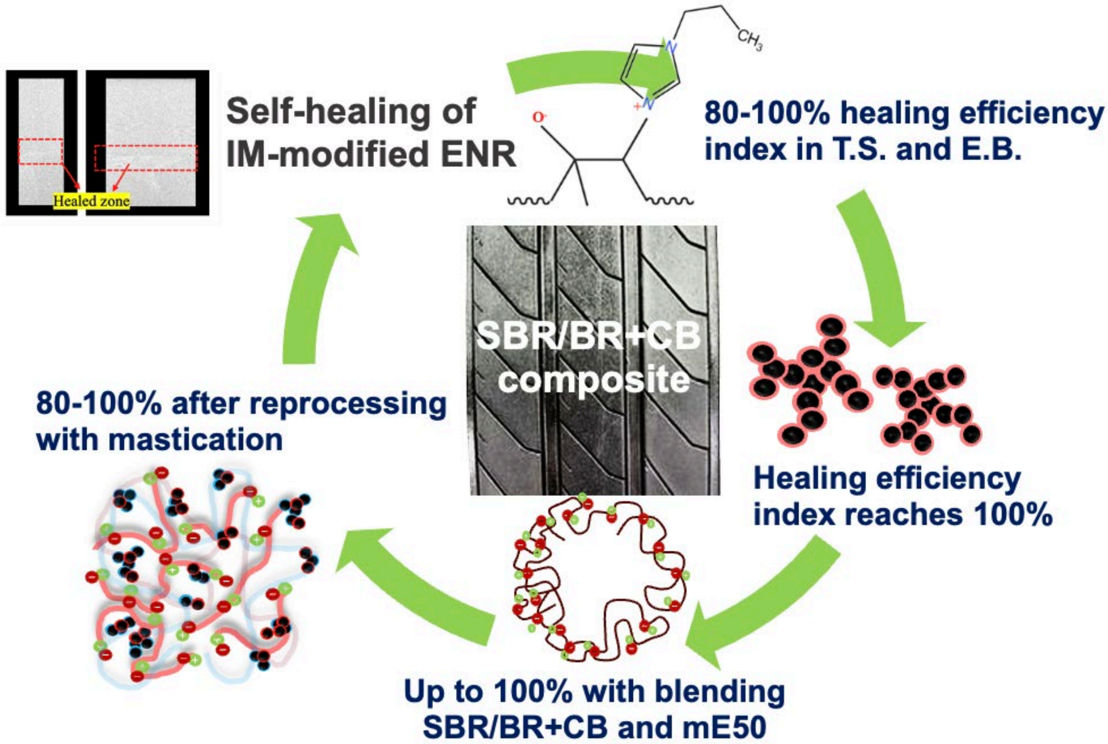
e-mail: yeampon.nak@kmutt.ac.th

[1]*Sustainable Polymer & Innovative Composite Materials Research Group, Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi (KMUTT), Thungkru, Bangkok 10140, Thailand*
[2]*Department of Advanced Materials and Surfaces, Empa-Swiss Federal Laboratories for Material Science and Technology, Ueberlandstrasse 129, 8600, Dübendorf, Switzerland*
[3]*Department of Mechanical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, 126 Pracha Uthit Rd., Bang Mod, Thung Khru, Bangkok 10140, Thailand*
[4]*Faculty of Science and Industrial Technology, Prince of Songkla University, Surat Thani Campus, Surat Thani 84000, Thailand*

Abstract

The development of sustainable elastomers with simultaneous mechanical robustness, self-healing ability, and recyclability remains a major challenge in advanced rubber engineering. This work presents a ligand-regulated dynamic network strategy based on epoxidized natural rubber containing 50 mol% epoxide groups (ENR-50), designed to generate self-healing, relaxation recovery, and reprocessable elastomeric composites for carbon black (CB)-reinforced systems. Imidazole (IM), 2,6-diaminopyridine (DP), and ferric ions (Fe^{3+}) were incorporated to construct hybrid dynamic networks consisting of reversible imidazolium–epoxy ionic interactions, Fe–O coordination crosslinks, and controlled intermolecular spacing. The Fe^{3+} coordination network enhanced mechanical stability, while IM promoted reversible ionic interactions that facilitated molecular rearrangement, stress redistribution, and autonomous healing. DP increased free volume and segmental mobility, enabling improved relaxation behavior without significantly disrupting the coordination network. The modified ENR was employed as a functional modifier in CB-filled styrene–butadiene rubber (SBR)/butadiene rubber (BR) blends. Optimized compounding sequences promoted effective rubber–filler interactions while preserving dynamic network mobility. Mechanical and dynamic mechanical analyses demonstrated that the optimized composites achieved tensile strengths approaching 10 MPa with elongation at break exceeding 400%, together with excellent recovery after damage and reprocessing. Temperature scanning stress relaxation (TSSR) revealed broadened relaxation spectra associated with thermally activated reversible dissociation and reconstruction of ionic and coordination bonds. Remarkably, the composites exhibited healing efficiencies exceeding 100% based on modulus recovery. These findings demonstrate that ligand-regulated ionic–coordination networks provide an effective pathway toward durable, self-healing, and recyclable elastomers for advanced tire and engineering rubber applications.

Scheme I


Self-healing of
IM-modified ENR
Healed zone
80-100% healing efficiency
index in T.S. and E.B.
SBR/BR+CB
composite
Healing efficiency
index reaches 100%
Up to 100% with blending
SBR/BR+CB and mE50
80-100% after reprocessing
with mastication

Biography

Name: Asst. Prof. Dr. Yeampon Nakaramontri

Title: Asst. Prof. Dr.

Affiliation: Department of Chemistry, Facult y of Science,
King Mongkut's University of Technology Thonburi

Country: Bangkok

Phone: +66828329854

E-mail: yeampon.nak@kmutt.ac.th

Personal History:
Yeampon Nakaramontri is an Assistant Professor in the Department of Chemistry, Faculty of Science at King Mongkut's University of Technology Thonburi. He received his B.Sc. in Rubber Technology and Ph.D. in Polymer Technology from Prince of Songkla University, completing his doctoral degree in 2016 at the Pattani campus. In 2018, he conducted postdoctoral research in collaboration with Prince of Songkla University and Osnabrück University of Applied Sciences before joining KMUTT as a lecturer. Dr. Nakaramontri is internationally recognized for his research on innovative natural rubber (NR) and advanced elastomeric materials. His work focuses on the development of sustainable and multifunctional rubber composites, particularly conductive NR, self-healing NR, disinfectant NR, biodegradable NR, piezoresistive and piezoelectric NR systems, thermoplastic–NR blends for 3D printing, controlled-release fertilizer systems, water-cured NR, and rubber waste recycling technologies. His multidisciplinary approach integrates polymer chemistry, materials science, engineering, agriculture, and biomedical applications to expand the versatility of natural rubber as a sustainable platform material. With support from the Department of Chemistry at KMUTT, he has authored more than 80 international publications and holds 15 petty patents related to rubber and polymer innovation. His research contributions span conductive rubber nanocomposites, dynamic crosslinking systems, thermoplastic elastomers, antibacterial rubber materials, and sustainable polymer technologies. He currently leads the "PSU × KMUTT Multidisciplinary Research & Innovation Project," coordinating collaborations among more than 50 researchers and lecturers from multidisciplinary backgrounds. Dr. Nakaramontri has received several prestigious awards for his scientific contributions, including Rising Star Awards from both the Faculty of Science and the university level at KMUTT, the Thailand Rising Star Award from the Polymer Society of Thailand in 2022, and the Thailand Rising Star Award from the Rubber-Elastomer Technology Association in 2024. Through his research, teaching, and industrial collaborations, he continues to promote the advancement of sustainable rubber technologies and circular materials innovation applications.

Research Keyword (3-5 keywords use commas to separate each word):
Rubber blend, Self-healing, Reprocessing, Tire application, Modified natural rubber