Investigation of the Formation of Styrene-Derivatives Pre-initiators in the Anionic Polymerization of Butadiene-Styrene Copolymers

Author: Piotr Babula

Abstract

The aim of this doctoral dissertation was to develop an effective method for α-functionalization at the chain initiation of styrene-butadiene copolymers (S-SBR) synthesized via anionic polymerization. Functionalization was achieved using styrene derivatives containing polar groups capable of interacting with inorganic fillers such as silica and carbon black, commonly used in rubber compounds for tire applications. The study focused on increasing the α-functionalization efficiency and assessing the impact of the functional group's location on the processing and dynamic properties of the resulting vulcanizates.

Pre-initiators were defined as reactive systems formed immediately prior to the actual initiation step. The research investigated the influence of synthesis parameters including the type and concentration of polar modifier, temperature, and initiator structure on the composition of the resulting oligomers and the effectiveness of functionalization. It was demonstrated that chemical structure of initiator and the presence of polar additives reducing initiator aggregation in hexane significantly improved functionalization outcomes.

The project was executed in three stages: batch laboratory scale using glass reactors, continuous laboratory scale, and technical scale in collaboration with Synthos S.A. in Oświęcim. Each stage built upon the findings of the previous one, enabling gradual process upscaling. The synthesized polymers were processed into rubber compounds, vulcanized, and characterized for their physical and dynamic properties. The developed conditions enabled an increase in α-functionalization efficiency from 20% to 92%. Precise functional group placement at the polymer chain's start was shown to improve the dynamic properties of vulcanizates, while requiring a lower amount of functional monomer compared to in-chain approaches.

This work provides valuable insights for designing functionalized S-SBR rubber for high-performance tire treads, with optimized rolling resistance, grip, and durability. The developed methodology was successfully scaled up for industrial implementation.