Title: Low-temperature sulfur vulcanization of diene rubbers

Authors:

Dr. Jakub Wręczycki: Lodz University of Technology, Faculty of Chemistry, Institute of Polymer and Dye Technology (RG: <u>https://www.researchgate.net/profile/Jakub-Wreczycki</u> / ORCID: <u>https://orcid.org/0000-0002-4817-7919</u>)

Prof. Dariusz M. Bieliński: Lodz University of Technology, Faculty of Chemistry, Institute of Polymer and Dye Technology (RG: <u>https://www.researchgate.net/profile/Dariusz-Bielinski</u> / ORCID: <u>https://orcid.org/0000-0003-0675-4594</u>)

Prof. Grzegorz Mlostoń: University of Lodz, Faculty of Chemistry, Department of Organic and Applied Chemistry (RG: <u>https://www.researchgate.net/profile/Grzegorz-Mloston</u> / ORCID: <u>https://orcid.org/0000-0003-3631-3239</u>)

Abstract:

The problem of rising electricity prices in recent times, by the still high dependence on the coal and oilbased raw materials and their price fluctuations has not bypassed the energy-intensive rubber industry either, which supplies products for many key sectors such as the automotive and aviation industries. From the point of view of energy savings in the rubber industry, it becomes legitimate to take measures to reduce the energy inputs needed to manufacture rubber products.

One of the potential solutions that could lead to this is lowering the temperature of the process (vulcanization) at which diene rubber products are manufactured. The production standards utilize mostly sulfur curing systems consisting of elemental sulfur, activators, and organic accelerators and are calibrated at high temperatures (at least 160 °C), to reduce the curing time and to enhance the production rates. The reduced temperature approach of sulfur vulcanization has many challenges, such as the need to find proper (reactive and safe) substances that effectively activate the vulcanizing system or activate themselves at lowered temperatures possibly without affecting vulcanization times (existing standards for production rates) and without changing the physical and chemical properties of the final rubber products. However, the outcome of this approach may be very beneficial including cost savings, reduced environmental impact (carbon footprint reduction), reduced risk of accidents due to high temperatures and volatile substances released, and more uniform properties of rubber products manufactured at lower temperatures.

As a result of our preliminary studies (June – August 2022) and later the research activity within the grant MINIATURA7 (September 2023 – September 2024) funded by the National Science Center in Poland we developed an approach that allows the reduce the temperature of sulfur vulcanization of diene rubbers significantly (up to 120 °C), by adding to the standard sulfur crosslinking system a fluoride anion (F^-) as a nucleophilic activator of elemental sulfur (crosslinking agent) (Figure 1.). The curing system was optimized (various fluoride salts and fluorides concentrations, various diene rubbers, and various fillers were tested) and enabled the maintenance of the structural parameters and mechanical parameters of rubbers at a comparable level, and in some cases even better than in the case of rubbers crosslinked at standard temperature (160 °C), without the addition of fluoride salts.

The proposed approach of introducing fluorides as an additional component of the standard sulfur crosslinking system based on elemental sulfur and organic accelerators represents a very simple, and at the same time effective solution of not only scientific but also practical importance, being an undoubted novelty in this research topic.



Figure 1. Graphical representation of the finished project idea (MINATURA 7).

Fundings:

The research work was carried out within the framework of the MINIATURA7 grant entitled: *The fluoride anion supported sulfur vulcanization of diene rubbers* (2023/07/X/ST5/00492) funded by the National Science Centre (Cracow, Poland).

Dissemination of the results:

Patent applications:

 P.442358. (submitted: September 2022). Wręczycki, J.; Bieliński, D.M.; Mlostoń, G. *In Polish*: Sposób modyfikacji siarkowej wulkanizacji kauczuków dienowych i mieszanek gumowych na bazie kauczuków dienowych.

Conference presentations:

 Wręczycki, J. Low-temperature sulfur vulcanization. 15th Fall Rubber Colloquium in Hanover (Germany) (10-12 September 2024).

Publications:

• Wręczycki, J., Bieliński, D.M., Gozdek, T., Kozanecki, M., Mlostoń, G. *Work title:* New perspective on the low-temperature sulfur vulcanization of diene rubbers – *in preparation*.