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**Synteza innowacyjnych funkcjonalizowanych
nanokompozytów styrenowo-butadienowych metodą
polimeryzacji w emulsji Pickeringa**

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DISSERTATION ABSTRACT

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| Title of doctoral dissertation: | Synthesis of innovative functionalized styrene-butadiene nanocomposites by Pickering emulsion polymerization. |
| Scientific discipline: | Chemical engineering |
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The dissertation undertook a study of the optimal conditions for carrying out the Pickering emulsion polymerization of styrene, and styrene and butadiene in the presence of anionic colloidal silica. The work was divided into three main stages, which were assumed to lead to the preparation of functionalized styrene and styrene-butadiene latex characterized by the corresponding morphology, which was analyzed by microscopic examination. Thus, the following stages were distinguished in the present study:

Stage 1: selection of optimal conditions for carrying out periodic polymerization of styrene using azoinitiator hydrochloride.

Stage 2: selection of a functionalizing compound that would make it possible to obtain latex by sodium persulfate-initiated Pickering emulsion polymerization.

Stage 3: redesigning the periodic to semi-continuous process and scaling up the polymerization of functionalized styrene latex. Pilot polymerization of functionalized styrene-butadiene latexes with different butadiene contents.

As a result of the stage 1 experiments, parameters affecting latex morphology and final conversion during the AAPH-initiated process were identified. These parameters include the type and particle size of the colloidal silica used, the pH of the aqueous phase, the process temperature and the percentage of colloidal silica with respect to the styrene used for polymerization. Based on the selected conditions of the process initiated with 2-2'-azobis(2-methylpropionamide) (AAPH), analogous polymerizations were carried out using sodium

persulfate obtaining significant coagulum contents already at the process stage. A completely different behavior was associated with the phenomenon of styrene functionalization, which is assumed to improve the compatibility of the hydrophobic polymer with hydrophilic and anionic colloidal silica as a result of the introduction of specific cationic groups derived from the AAPH initiator. Thus, a study was undertaken towards the possibility of functionalizing latex in-chain (in-chain) by selecting a suitable monomer that would act as an adhesion promoter to colloidal silica. For this purpose, the selected reaction system initiated with sodium persulfate, or an equimolar mixture of sodium persulfate and AAPH was tested with various monomers functionalized in the experiments of stage 2. The selection of monomers was based on the positive effect of azoinitiator hydrochloride on the compatibility of the resulting latex with colloidal silica. Thus, monomers were selected that contained in their structure:

- a primary amine group,
- an arylammonium group,
- an amino group, and a sulfonic group,
- an amide group that could hydrolyze to a carboxylic acid under process conditions,
- an amide group that readily hydrolyzes to a primary amine.

Taking into account the low price of sodium persulfate and its availability, the next experiments of redesigning the periodic process to a semi-continuous process with scaling-up were carried out according to the developed formulation with the selected monomer in stage 3. The developed formulation in the periodic process was successfully redesigned to a semi-continuous process obtaining the correct particle size parameters, and the appropriate morphology confirmed by microscopic examination. The redesigned functionalized latex was scaled up from 200 g to 7000 g scale on a 10 L pilot plant. Scaling up the process successfully yielded a polystyrene latex with the correct morphology. In subsequent trials, butadiene was introduced into the formulation at various concentrations obtaining a successfully functionalized styrene-butadiene latexes on the scale of 7000 g in a rigid version and a version with moderate rigidity. In summary, functionalized sodium persulfate-initiated latexes were successfully obtained on a 10 L pilot scale. The developed Pickering emulsion polymerization formulation has implementation potential as a compounding component in both already recognized applications of styrene-butadiene latexes and in potential new technical applications where functionalization of styrene and styrene-butadiene copolymer may be important.