Applying the electron-beam preirradiation method in air the cation-exchanger fabric (CEF) containing sulfonic acid (R-SO$_3$H) groups was prepared by graft copolymerization of sodium styrenesulfonate with acrylic acid onto nonwoven polypropylene fabric. The effect of reaction conditions on the grafting yield and reaction mechanism was examined. It was found that the received CEF contains groups of strong acid (R-SO$_3$H) and weak acid (R-COOH) in almost equal proportion.

The ion-exchange properties of the CEF towards Cu(II) and Co(II) ions were investigated depending on the form of the CEF and a pH of the solution. It was shown that the utilization of the CEF in Na-form allows to make the best use of its ion-exchange capacity.

Electron beam irradiation; Preirradiation graft copolymerization; Polypropylene fabric; Sodium styrenesulfonate; Cation-exchanger fabric.

**INTRODUCTION**

The production of sorption-active natural and synthetic fibers and textile materials is of both great scientific and practical interest. The application of economical and ecologically clean radiation technologies for this purpose is now under the intent attention of researchers [1,2,3].
The CEF with strong acid cation-exchange groups are widely used in various domains [4,5], therefore this work aims to synthesize the CEF with sulfonate functional groups by means of radiation-induced graft copolymerization of acrylic acid and sodium styrenesulfonate onto nonwoven polypropylene and to characterize its exchange properties.

1. EXPERIMENTAL

1.1. Materials

Commercial nonwoven polypropylene fabric – PP – (120g/m², degree of crystallinity of 65%, Toray-Saehan Co.Ltd) was used for grafting. Reagent grade acrylic acid -Aa- (Junsei Chemical Co.Ltd), sodium styrenesulfonate –SSS- (Tokyo Kasei Kogyo Co.Ltd), Mohr’s salt (Merck, Germany) were used as received.

1.2. Graft copolymerization procedure

Preirradiation grafting technique was employed for graft copolymerization [6]. The irradiated fiber was weighed and immersed into a glass flask with the monomer solution (Aa:SSS = 0.1 M : 0.1M in 100 ml of water) and inhibitor (Mohr’s salt), which was purged then by bubbling nitrogen.

The degree of cografting was calculated from the weight gain:

\[ \text{DG\%} = \left( \frac{W_i - W_o}{W_o} \right) \times 100 \]

where \( W_0 \) and \( W_i \) are the weight (g) of original and grafted fabric, respectively.

The preparation scheme is shown in Fig. 1.

![Chemical reaction diagram](image)

Fig. 1. Preparation of cation-exchanger fabric by radiation-induced graft copolymerization of sodium styrenesulfonate with acrylic acid onto nonwoven polypropylene fabric.

1.3. Fabric characterization

1.3.1. FT-IR analysis

In order to confirm the introduction of functional groups onto PP fabric the IR spectra of modified fabric were obtained from FT-IR spectrometer (Perkin-Elmer, 1725).

1.3.2. Cation-exchange capacity

Total exchange capacity of the modified fabric, which reflects general content of functional groups grafted onto PP trunk, was determined by backward titration method. The number of sulfonic acid and carboxylic acid groups was evaluated by sorption of Cu (II) and Co(II) ions onto the Aa-SSS grafted fabric depending on a pH of the Me(II) ion solutions and the form of the CEF.
2. RESULTS AND DISCUSSION

2.1. Copolymerization process

The CEF containing R-SO_3H groups was prepared by radiation-induced graft copolymerization of acrylic acid and sodium styrenesulfonate monomers onto PP fabric. Many factors affect the radiation grafting process of binary monomer mixture. Among them, investigated here, are total exposure dose, reaction time and temperature, concentration of inhibitor of homopolymerization (Mohr’s salt). The effects of these factors are considered and determined from the viewpoint of obtaining cation-exchanger fabric with reasonable grafting degree.

When polypropylene fabric is irradiated in the presence of air, mainly hydroperoxides are formed onto the polymeric backbone. These hydroperoxides decompose upon heating to generate hydroxyl radicals (OH), which initiate the homopolymerization process, and macroradicals (PPO), which offer sites for grafting [6]. To overcome homopolymerization some small amount of a transition metal salt is usually used as inhibitor [7,8]. Fig. 2 shows the effect of Mohr’s salt concentration on the Aa-SSS grafting degree. The effect of absorbed dose on the grafting degree is shown in Fig. 3.

It should be noted, that in the IR spectra of the samples, irradiated with doses less than 40.3 kGy, only a characteristic peak at 1738 cm\(^{-1}\) assigned to -C=O group of acrylic acid was observed, while the IR spectra of the samples, irradiated with more higher doses, exhibited also characteristic peaks (at 1200 cm\(^{-1}\), 1050 cm\(^{-1}\) and 650 cm\(^{-1}\)) attributed to sulfonic acid (R-SO_3H).

The effect of reaction time and reaction temperature on the degree of graft copolymerization is shown in Fig. 4.

It can be seen that the kinetic curve of graft copolymerization of monomer mixture at 50°C consists of a few stages – (0-10h) and (12-32h). Analysis of the IR spectra of the samples of mentioned stages allowed us to judge about the graft copolymerization mechanism. The fact that there were no another characteristic peak than one at 1738 cm\(^{-1}\) due to C=O group in the IR spectra of the former stage, and there were observed two kinds of peaks attributed to acrylic acid (1738 cm\(^{-1}\)) and sulfonic acid (1200-1150; 950, 650 cm\(^{-1}\)) in the IR spectra of the latter stage’s samples testifies that the process, beginning with the grafting of acrylic acid monomers onto PP trunk, goes on after that by the inclusion of the SSS monomers into the growing chains. The maximal degree of grafting (155%) was obtained under the following conditions – absorbed dose 70.5 KGY, reaction temperature 50°C and reaction time 32h.
2.2. Cation-exchange properties

The CEF prepared by radiation-induced graft copolymerization of SSS and Aa onto the nonwoven PP fabric represents a bifunctional cation-exchanger carrying two types of functional groups - both carboxylate and sulfonate ones. Fig. 5 shows a relationship between the total exchange capacity of the CEF, which reflects general content of functional groups, and the degree of graft copolymerization. Maximum value of the total exchange capacity of 4.30 meq/g was obtained for the CEF with 155% grafting degree.

Fig. 4. Effect of reaction time on the Aa-SSS grafting degree (in the presence of 10^{-2} w% Mohr’s salt)  
Fig. 5. Dependence of the total exchange capacity of Aa-SSS grafted fabric upon the degree of graft copolymerization

It is well known that cation-exchange capacity of a strong acid (as sulfonic acid) is independent of a solution pH, while this value of a weak acid (as carboxylic one) is strongly influenced by the solution acidity. That is why the evaluation of the functional group contents due to sulfonic acid and carboxylic acid is extremely important for the practical application of obtained CEF. Fig. 6 shows the kinetic curve of Cu (II) and Co(II) ions sorption from acidic solution (pH~4) onto the CEF in the H-form.

It can be seen that the cation-exchange capacity of investigated samples in acidic solution twofold lower than their total exchange capacity. If we consider the mentioned above fact that the carboxylic acid groups are weakly dissociated in acidic solution and their hydrogen ions aren’t available for exchange we may conclude that the CEF obtained by radiation-induced graft copolymerization of SSS and Aa acid contains both strong acid (R-SO_{3}H) and week acid (R-COOH) groups in almost equal proportion and grafted chains probably have a regular structure: PP-Aa-SSS-Aa-SSS-.

The binding properties of obtained CEF in Na- form towards Co(II) ions from basic solution (pH~8) are shown in Fig. 7. It can be seen that the CEF in Na- form binds Co (II) ions according to its total exchange capacity.
Fig. 6. Sorption rates of Me(II) ions on the CEF samples in H-form with different total exchange capacity values from acidic solution (pH=4)

CONCLUSIONS
1. The cation-exchanger PP fabric with strong acid (R-SO3H) groups has been prepared by radiation-induced graft copolymerization of sodium styrene sulfonate and acrylic acid onto the nonwoven PP fabric in one experimental step.
2. The main factors affected the radiation grafting process of binary monomer mixture onto PP fabric has been considered. Obtained data allowed us to judge about the mechanism of graft copolymerization: the process, beginning with the grafting of acrylic acid monomers onto PP backbone, goes on after that by the inclusion of the SSS monomers into the growing chains.
3. The total exchange capacity of the grafted fabric versus its grafting degree has been evaluated.
4. Obtained CEF contains strong acid (R-SO3H) and week acid (R-COOH) groups in almost equal proportion and exhibits strong acid behaviour over the entire pH range in half its total exchange capacity.
5. The application of grafted fabric in Na-form in basic solution allows to utilize its total exchange capacity in full volume.

REFERENCES