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PRODUCTION OF SORPTION ACTIVE POLYPROPYLENE FABRICS WITH SULFONIC ACID GROUPS BY RADIATION-INDUCED MODIFICATION OF POLYMER SURFACE

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Sorption active material carrying sulfonic acid groups was synthesized by radiation-induced graft polymerization of styrene monomer onto the surface of non-woven polypropylene fabric followed by sulfonation of grafted polystyrene chains. The effect of the main experimental parameters on styrene grafting degree (absorbed dose, monomer concentration, reaction time) was investigated. It was found that sulfonation degree of the grafted polystyrene chains with 5% chlorosulfonic acid at room temperature depends on the reaction time and reaches 80% for the samples with a medium value of styrene grafting degree. Sorption active polypropylene fabrics with sulfonic acid group densities of 3.5–5 meq/g were obtained.

INTRODUCTION

Polypropylene (PP) fibers and nonwoven fabrics have been frequently used as base polymer matrix for synthesis of various sorption active materials. This is because of their low cost, saturated structure, high radiation and chemical resistance, excellent mechanical properties of PP matrix and highly developed specific surface [1, 2].

To obtain sorption active PP materials the radiation-induced graft polymerization method can be used. When polymer matrix is subjected to high energy irradiation (electron beam accelerators, γ-rays sources, plasma treatment), the active cites are formed on the polymer surface. They can initiate graft polymerization of a proper monomer [3–7]. As a result of graft polymerization reaction, the surface of the primary polymer matrix becomes covered by nano(micro)-chains of the grafted monomer. Density and chemical nature of the functional group of the grafted monomer as well as the degree of modification of the primary polymer matrix can vary depending on the experimental condition so that to tailor the resulting adsorbent for the concrete technological tasks.

Two main methods in radiation-induced graft polymerization have been developed for polymer surface modification: (1) simultaneous (or mutual) method and (2) pre-irradiation (or post-irradiation) method [3–7].

In the simultaneous irradiation method a polymer matrix is exposed to high energy irradiation in the presence of a monomer, so that active sites are formed on both polymer backbone and monomer units. Irradiation can be carried out in inert atmosphere (e.g. N_2) or under vacuum. Pre-irradiation method involves a combination of two steps: a polymer backbone is first exposed to ionizing irradiation in vacuum, air or inert atmosphere to generate active cites and then it contacts with monomer units in inert atmosphere.

From the practical viewpoint, it is extremely interesting to prepare sorption-active PP fibers and fabrics with strong sulfonic acid group [2, 5, 7, 8].

Several approaches can be used for this purpose: direct grafting of a monomer with sulfonate group or grafting of a precursor-monomer (for example, glycidyl methacrylate or styrene) with subsequent sulfonation of grafted chains.

There is a vinyl monomer with sulfonic acid group (i.e. sodium styrenesulfonate); however, graft polymerization of this monomer onto PP matrix has failed [9, 10]. Only copolymerization of two monomers - acrylic acid and sodium styrenesulfonate onto the PP surface has led to a positive result [10].

Glycidyl methacrylate (GMA), an epoxy-group containing monomer, is widely used as a precursor-monomer for production of polymeric adsorbents of variety applications on the base of membranes, films, fibers and fabrics [11, 12]. It also has been used for synthesis of PP fabrics with sulfonic acid functional group [13].

In the current paper we considered the graft polymerization of styrene as a precursor-monomer. Radiation-induced graft polymerization of styrene with subsequent sulfonation of the grafted polystyrene chains was used to produce PP fabric with sulfonic acid groups. The influence of irradiation and experimental conditions

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(absorbed dose, styrene concentration, reaction time) on the grafting yield and peculiarities of sulfonation process are discussed.

EXPERIMENTAL

Materials. Commercial nonwoven polypropylene (PP) fabric with a thickness of 0.7 mm and a density of 146 g/m^2 obtained from Saehan felt Co. Ltd was used as a trunk polymer for grafting. Reagent grade styrene monomer (St) and ethanol (Aldrich Co.) was used without further purification. Reagent grade chlorosulfonic acid and dichloromethane (Kanto Chemical) were used for the sulfonation without further purification. Other chemicals were of reagent grade.

Graft copolymerization procedure. The pre-irradiation grafting method was carried out in air for the graft polymerization of styrene monomer onto PP fabric. The PP fabric was cut into 50x50 mm quadrates, cleaned with acetone for 24 h and then dried at 80^{o}C for several hours before being weighted. The prepared samples were irradiated with an electron beam from an ELV-05 electron beam accelerator (BINP, Russia) with an accelerated energy of 0.7 MeV to doses ranging from 40 to 100 kGy at ambient temperature. The irradiated fabric was immersed in a 250 ml glass flask with the monomer solution (styrene in ethanol). Then the flask was purged using nitrogen gas, sealed, and placed in a water bath that was maintained at 50^{o}C constant temperature for different time periods. At the end of this stipulated time period, the grafted PP fabric was removed from the solution, washed thoroughly with hot benzene in Sohxlet over 8 h to remove any homopolymers and unreacted monomers. Finally, the grafted films were dried in a vacuum oven at 80^{o}C until they reached a constant weight. The degree of grafting (DG) was calculated from the weight gain: DG (%) = $[(W_1\text{-}W_0)/W_0]$ x 100 where W_0 and W_1 are the weights (g) of the original and grafted films, respectively.

Sulfonation procedure. The PP fabric with grafted poly-styrene chains (PP-g-PSt) was sulfonated at room temperature with a 5% solution of chlorosulfonic acid in dichloromethane (DCM) for different time periods. Before sulfonation the grafted samples were pre-treated in DCM for 30 min. After sulfonation reaction the studied samples were repeatedly washed with fresh DCM for 5 h to reduce the content of residual acid, neutralized with 0.5 M $NaHCO_3$ and then hydrolyzed overnight at 30^{o}C. To obtain cation exchange fabric in H$^+$-form the sulfonated samples were regenerated with 0.1 M HCl solution and then washed thoroughly with deionized water and dried. The ion exchange capacity (IEC), reflecting the actual density of the incorporated sulfonic acid groups, was determined by titration experiment.

Ion exchange characteristics. The ion exchange capacity (mEq/g) of the synthesized PP fabrics was determined through backward titration experiments. The sulfonated PP-g-PSt sample was placed into a flask with 50 ml of a saturated NaCl solution and equilibrated for 24 h. The equilibrated solution was titrated to the phenolphthalein end point with 0.1 N NaOH solution using TITRONIC 97/50 auto burette.

The IEC value of the sulfonated fabric was calculated using the following equation: IEC (meq/g) = $0.1xV_{NaOH}/W_d$ where, V_{NaOH} is the volume of NaOH solution that was consumed during titration, and W_d is the weight (g) of the dry membrane in the H$^+$ form.

RESULTS AND DISCUSSION

Sorption active polymer fabrics, carrying sulfonic acid groups, have been synthesized by radiation-induced graft polymerization of the styrene onto nonwoven PP fabric followed by the sulfonation reaction (Fig. 1). This method has been widely studied over the last decade for synthesis of sulfonic acid proton exchange membranes for fuel cells based on hydrocarbon and fluorocarbon polymer films [5–7]. However, there are only a few publications on peculiarities of both radiation-induced graft polymerization of styrene onto PP nonwoven fabric and subsequent sulfonation of grafted PSt chains [2, 14, 15]. None of these papers considered issues concerning the optimal density of grafted PSt chains, efficiency of sulfonation of benzene rings of the PSt chains, and stability of the functional groups in adsorption processes. The diversity of problems solved using polymeric adsorbents necessitates further search for the best synthesis procedures and a comprehensive study on the properties of the materials prepared.

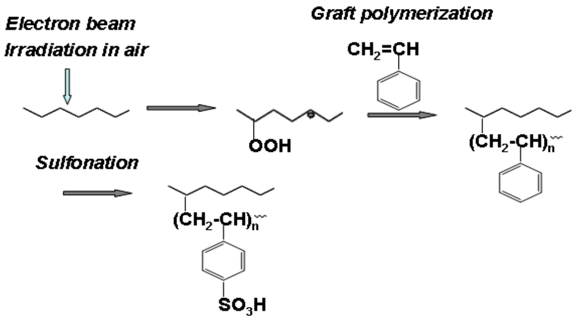

Fig. 1. Radiation-induced graft polymerization of styrene onto PP nonwoven fabric

Graft polymerization of styrene onto nonwoven polypropylene fabric. To investigate the graft polymerization of styrene onto nonwoven PP fabric, the reaction temperature of 50°C was chosen. The other parameters affected this reaction, namely, monomer concentration, adsorption dose, reaction time have been investigated to obtain PP fabric with the reasonable styrene grafting degree.

Effect of monomer concentration. The influence of monomer concentration on the degree of styrene graft polymerization is shown in Fig. 2. Among different diluents used for styrene we used ethanol. The curve of grafting degree against monomer concentration has a sharp peak at monomer concentration of 20%. Similar behavior of grafting curve against monomer concentration was observed in [14] where it was explained in terms of a Trommsdorff effect.

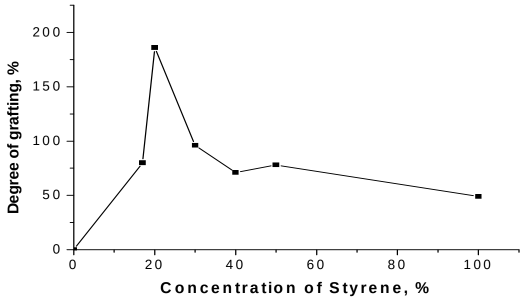

Fig. 2. Effect of styrene concentration on the degree of grafting. Reaction time 2 h, reaction temperature 50°C, absorbed dose 100 kGy

Effect of absorbed dose. The influence of absorbed dose on the extent of the styrene grafting process from 20% monomer solution is shown in Fig. 3. Under chosen reaction conditions the degree of graft polymerization linearly increases with the increase of absorbed dose from 40 to 100 kGy. It can be explained by the fact that the increase in absorbed dose causes an increase in the number of reactive sites for the grafting.

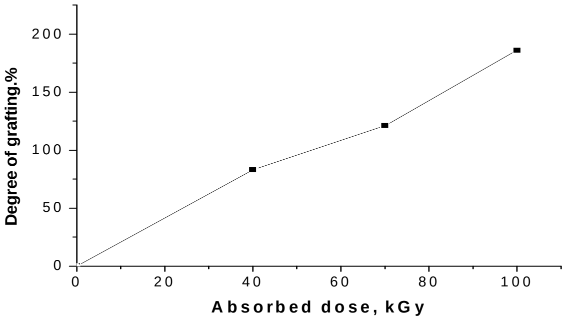

Fig. 3. Effect of absorbed dose on the degree of styrene grafting. Styrene concentration 20%, reaction time 2 h, reaction temperature 50°C

Effect of reaction time. Fig. 4 shows the variation in the degree of styrene graft polymerization on PP fabric with respect to the reaction time. The rate of grafting grows significantly during the initial 2–3 h and then levels off.

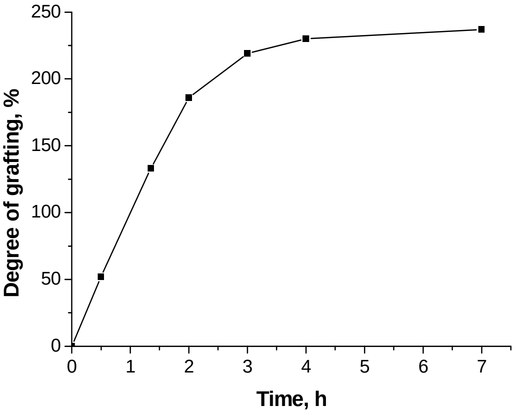

Fig. 4. Effect of reaction time on the degree of grafting. Absorbed dose 100 kGy, styrene concentration 20%, reaction temperature 50°C

Thus, varying such experimental parameters as absorbed dose, monomer concentration, reaction time, the styrene-grafted polypropylene fabrics with a wide range of polystyrene-chain density have been obtained (Fig. 5).

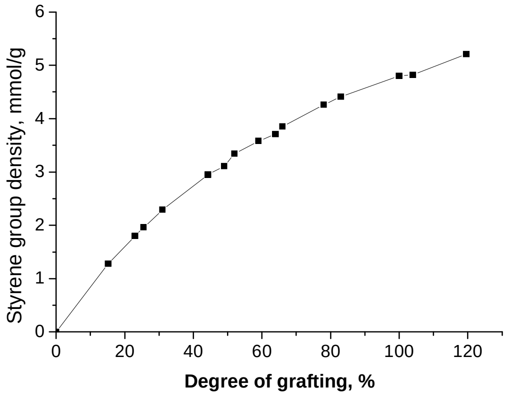

Fig. 5. Properties of the styrene-grafted PP nonwoven fabrics used for sulfonation experiments

Sulfonation of grafted polystyrene chains. To function as a sorption active material the PP fabric with PSt grafted chains need to undergo further sulfonation process. Only one sulfonic acid group may be attached to the carbon of an aromatic ring, so in the case of full sulfonation conversion, the number of the sulfonic acid groups should be equal to the number of the grafted styrene chains.

There are several sulfonating agents used for introduction of sulfonic acid groups into the benzene rings of the grafted PSt chains: concentrated sulfuric acid, chlorosulfonic acid in methylene chloride, a mixture of sulfuric acid and chlorosulfonic acid, acetyl sulfate solution, dioxane-SO_3 complex, pyridine-SO_3 complex, etc. [2, 8, 16, 17].

From the practical view point the moderate experimental conditions (low temperature and low concentration of sulfonating agent) are more preferable because strong acids of high concentration and high temperature cause side reactions and degradation of the PP matrix [16, 17].

Chlorosulfonic acid solutions of 5% in dichloromethane and room temperature were chosen for the experimental study.

Several samples with a medium value of styrene grafting degree (70–120%) were immersed in dichloromethane for swelling (30 min) and then treated with acidic solution for different time periods (5–100 min). The density of the incorporated sulfonic acid groups was determined through backward titration experiment (IEC value). The sulfonation degree (percent of conversion) was calculated as a ratio of the sulfonic acid groups density (IEC value) to the styrene group density for the investigated sample (from Fig. 5).

The sulfonation degree curve with respect to the sulfonation time is shown in Fig. 6. It can be clearly seen from this figure that the maximum sulfonation degree of 82% can be reached within the time interval of 60–90 min; when the sulfonation time was greater than 90 min, the sulfonation degree decreased due to the side reactions (desulfonation and sulfone formation) [16, 17]. Therefore, sulfonation with 5% chlorosulfonic acid at 25°C for 60–90 min is recommended for the PP nonwoven fabric with a medium value of styrene grafting. These conditions allow to synthesize sorption active polypropylene fabrics with the sulfonic acid group density (or the IEC value) of 3.5–5 meq/g.

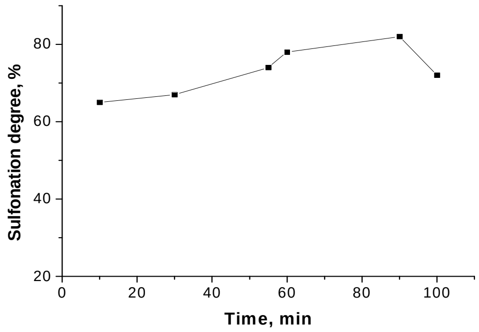

Fig. 6. Effect of time on sulfonation degree of PP-g-PSt fabrics with a medium value of styrene grafting degree. Chlorosulfonic acid in dichloromethane (5%), room temperature

This parameter is higher than the IEC of the PP fabrics with sulfonic acid groups synthesized by radiation grafting of the vinyl monomer with sulfonic acid group (sodium styrene-sulfonate) (0.5–2.13 meq/g) [10] or radiation grafting of GMA as a precursor-monomer and subsequent sulfonation of polyGMA grafted chains (1–2.5 meq/g) [13].

CONCLUSIONS

Sorption active polypropylene fabrics with sulfonic acid functional groups have been prepared by radiation-induced graft polymerization of styrene using pre-irradiation method in air followed by sulfonation of grafted polystyrene chains with chlorosulfonic acid at room temperature.

Varying such experimental parameters as absorbed dose, monomer concentration and reaction time, the styrene grafted polypropylene fabrics with a wide range of styrene-chain density have been synthesized. Subsequent modification consisted in the incorporation of the sulfonic acid groups by reacting of the benzene rings of the PSt grafted chains with 5% chlorosulfonic acid in dichloromethane at room temperature for 60–100 min allowed to obtained sorption active polypropylene fabrics with high value of sulfonic acid group density – 3.5–5 meq/g.

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Використання радіаційно-індукованої полімеризації для отримання сорбційно-активних поліпропіленових тканин з сульфокислотними групами

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Радіаційно-індукована прищеплювальна полімеризація стиролу на неткану поліпропіленову тканину з подальшим сульфуванням прищеплених ланцюгів полістиролу була використана для синтезу сорбційно-активного матеріалу. Проведено дослідження впливу основних експериментальних параметрів (поглинена доза, концентрація мономера, час реакції) на ступінь прищеплювальної полімеризації стиролу. Встановлено, що ефективність сульфування прищеплених ланцюгів полістиролу при кімнатній температурі в 5% розчині хлорсульфонової кислоти залежить від часу реакції і для зразків з середніми ступенями прищеплення досягає 80%. Були синтезовані сорбційно-активні поліпропіленові тканини з щільністю кислотних груп 3,5–5 мг-екв/г.

Использование радиационно-индуцированной полимеризации для получения сорбционно-активных полипропиленовых тканей с сульфокислотными группами

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Радиационно-индуцированная прививочная полимеризация стирола на нетканной полипропиленовой материи с последующим сульфированием привитых цепей полистирола была использована для синтеза сорбционно-активного материала. Проведено исследование влияния основных экспериментальных параметров (поглощенная доза, концентрация мономера, время реакции) на степень прививочной полимеризации стирола. Установлено, что эффективность сульфирования привитых цепей полистирола при комнатной температуре в 5% растворе хлорсульфоновой кислоты зависит от времени реакции и для образцов со средними степенями прививки достигает 80%. Были синтезированы сорбционно-активные полипропиленовые ткани с плотностью кислотных групп 3,5–5 мг-экв/г.