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Surface Modification of Polypropylene Membrane by γ Irradiation Methods and their Solutes Permeation Behaviors

J. K. Shim, S. H. Lee, O. H. Kwon Y. M. Lee, Y. C. Nho[*]
Department of Industrial Chemistry, College of Engineering,
Hanyang University, [*]Korea Atomic Energy Research Institute

1. Introduction

The conventional grafting polymerization technique requires chemically reactive groups on the surface as well as on the polymer chains. For this reason, a series of prefunctionalization steps are necessary for covalent grafting. The surface prefunctionalizational technique for grafting can be used to ionization radiation, UV, plasma, ion beam or chemical initiators. Of these techniques, radiation method is one of the useful methods because of uniform and rapid creation of active radical sites without catalytic contamination in grafted samples. If the diffusion of monomer into polymer is large enough to come to the inside of polymer substrate, a homogeneous and uniform grafting reaction can be carried out throughout the whole polymer substrate. Radiation-induced grafting method may attach specific functional moieties to a polymeric substrate, such as preirradiation and simultaneous irradiation. The former is irradiated at backbone polymer in vacuum or nitrogen gas and air, and then subsequent monomer grafting by trapped or peroxy radicals, while the latter is irradiated at backbone polymer in the presence of the monomer. Therefore, radiation-induced polymerization can be used to modification of the chemical and physical properties of the polymeric materials and has attracted considerable interest because it imparts desirable properties such as blood compatibility. membrane quality, ion excahnge, dyeability, protein adsorption, and immobilization of bioactive materials. Synthesizing biocompatible materials by radiation method such as preirradiation or simultaneous irradiation has often used γ-rays to graft hydrophilic monomers onto hydrophobic polymer substrates.

In this work, in attempt to produce surfaces that show low levels of anti-fouling of bovine serum albumin(BSA) solutions, hydroxyethyl methacrylate(HEMA) was grafted polypropylene membrane surfaces by preirradiation technique. The anti-fouling effect of the polypropylene membrane after grafting was examined by permeation BSA solution.

2. EXPERIMENTAL

Commercial polypropylene(PP) membrane(Celgard 2400, Hoechst Korea) was used as a substrate for graft polymerization. The porous membrane has these properties, the thickness is 22.9~27.9m, the pore size is 50x125nm and the percentage porosity is 28~40%. It was washed with methanol and dried in vacuum oven at 40C for 2 days to remove additives before use. Hydroxyethyl methacrylate(HEMA) was supplied from Aldrich Chemical Co.(USA) and used without futher treatment. Bovine serum albumin(BSA) was supplied from Sigma Chemical Co.(fraction V, USA). All other chemicals were reagent grade or higher. The cleaned PP membrane was cut into 10×10 cm pieces and dried in a vacuum to constant weight at 60℃ for 24 h. It was stored in a desiccator until use.

The γ-rays from Co-60 sources were carried out at an exposure rate of 4.51 kGy/h in the presence of air to a total dose of 10 - 30 kGy.

The preirradiated PP membranes were stored in refrigerator kept at -130℃ immediately after irradiation until the grafting reaction. The grafting experiments were conducted in a glass ampoule having a 2.5×15 cm dimensions with cock, the methanol being added first, followed by monomer to a total volume of 20 ml. The preirradiated PP membranes were immersed in the monomer solution, purged by bubbling nitrogen gas for 10 min before and after immersion sample for the purpose of degassing and then sealed in a glass ampoule. The grafting reaction was carried out by placing the glass ampoules with monomer solution in a water bath at the relevant temperature. This graft copolymerization was initiated by trapped radicals on the PP membranes. After graft reaction,, the grafted PP membranes were quickly taken out of the monomer solution in a glass ampoule and washed in a pure water with stirring for 5 h to remove the unreacted remaining monomers or homopolymers. And then the grafted PP membranes dried in a vacuum oven to constant weight at 60℃ for 24 h.

For UF characterization, stirred test cells with 50 or 200ml volume and 13.4 or 28.7cm^2 membrane area, respectively, were used(Model 8050 & 8200, Amicon Div., W.R. Grace, MA) at 297K. Membrane were immersed in methanol for 1hour, then the solution was replaced with deionized water. Water fluxes measured by pre-determined time until a stable value J_{w1}, was observed. The permeate fluxes at the beginning(J_{p1}) and end(J_{p2}) of this period for BSA solutions(0.5wt% aqueous solutions) were measured by pre-determined time and protein concentrations were analyzed with the UV spectrophotometer at 280nm. All permeation behaviors were conducted at 200kPa. The water fluxes J_{w2} measured after briefly rinsed with deionized water to remove BSA from the membrane for 5 min. in the retentate channel.

3. RESULTS AND DISCUSSION

Among the synthetic polymers, polypropylene is superior to chemical and electrical properties as well as physical properties such as tensile strength, hardness, impact strength, and so on. Therefore polypropylene is widely used fiber, rough, household goods, and packing materials. And also, in recent, it is used medical uses such as disposable syringe and oxygernator because of excellent transparency and processing as well as nontoxic. For using to aims above as described, it needs to modify polypropylene surface to having hydrophilic functional groups on polymeric substrate surface. However, it is difficult to modify polypropylene to hydrophilic surfaces because polypropylene is inactive chemically. It needs to active sites for modification of polymer surface because polypropylene is hydrophobic, the radiation can make homogeneous active sites on polymer surface without contamination by catalyst because of useless one. Thus grafting technique by radiation can be modified homogeneously polypropylene surfaces as well as inner sides according to circumstances. When polypropylene is irradiated in the presence of air, the free radicals and peroxides such as diperoxides or hydroperoxides capable of initiating the grafting reaction can be formed and the yields of those are different depending on the presence of oxygen. The backbone of polypropylene has a hydrogen atom on a tertiary carbon atom, and this tertiary hydrogen atom is involved in the degradation of a macromolecular chain when polypropylene are irradiated.

A hydrophobic membrane can be retained resistant to protein adsorption by grafting a hydrophilic polymer. These functionalities can be acquired by selecting different functional monomers. In membrane areas, the surface modification of polymers has been focused on preventing membranes fouling from the adsorption of retained particles, salts, macromolecules, etc. which cause the flux decline.

The advancing and receding contact angles for original PP and PP-g-HEMA membranes decreased with increasing grafting yield. The grafting yield of PP membranes increased with γ-irradiation dosage, reaction temperature and reaction time.