Radiation-Induced Grafting of Regenerated Cellulose Hollow-Fiber Membranes

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Synopsis

Gamma ray radiation-induced grafting was carried out on regenerated cellulose hollow-fiber membranes as the substrate polymer and employing a number of monomer and solvent systems. The monomers used include styrene, maleic acid, acrylonitrile, acrylamide, and acrylic acid. Characterization of the graft copolymers was done by measuring their tensile properties in terms of breaking loads and breaking extensions. Permeation properties of the modified membranes were also assessed by measuring the water flux of each membrane. Membranes grafted with styrene showed improved tensile and permeation properties, while co-irradiation graftings using acrylamide and acrylic acid as monomer only showed improved tensile properties but not the permeation properties of virgin membranes. For a given monomer, the pre-irradiation grafting technique generally produced membranes with lower water fluxes than those produced using co-irradiation grafting.

INTRODUCTION

Grafting is one of the most commonly used techniques to modify the properties of preformed polymers. Most of the work done in this field has been in the textile, paper, and rubber industries. However, with the rapid development of membrane technology, a number of workers[1-8] have used the technique to modify the properties of the existing membranes or the polymer before casting of the membranes. This work aims to improve the properties (both physical and transport) of regenerated cellulose hollow-fiber membranes using the radiation-induced grafting technique, employing various monomer and solvent systems.

EXPERIMENTAL

Materials

Cuprophan hollow-fiber membranes, GF180M, manufactured by Gambro, were used as a basis of this study. These membranes were sealed in a polyurethane resin and surrounded by a polystyrene–acrylonitrile shell with 2 side arms. This unit holds approximately 13,000 fibers, having a total active area of 1.8 m^2. Each fiber has a wall thickness of about 8 μm and an internal diameter lumen of 200 μm. The untreated membranes are reported to have a molecular weight cutoff of 5000 daltons. A schematic drawing of the membrane module is given in Figure 1.

Keys:
1. Polycarbonate end caps;
2. Polyurethane seal (or potting material);
3. Polystyrene-acrylonitrile shell;
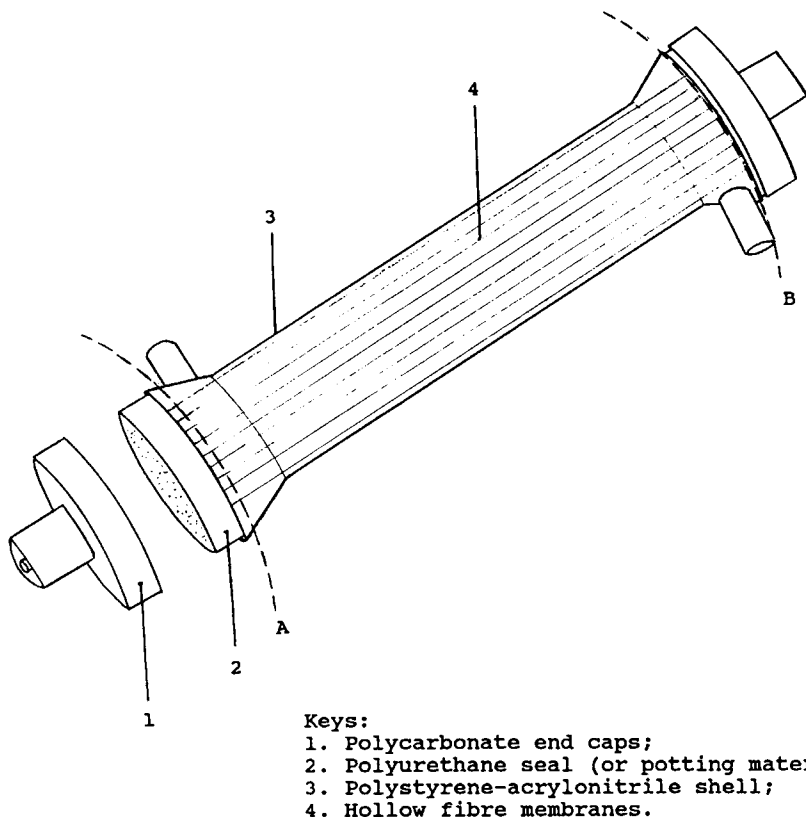4. Hollow fibre membranes.

Fig. 1.   Schematic drawing of the hollow-fiber membranes in a cartridge.

Reagents used for grafting include reagent grade styrene, acrylonitrile, acryl-amide, maleic acid, acrylic acid, methanol, and benzene. Styrene was purified by washing with 10% NaOH solution followed by distilled water and allowed to dry overnight in anhydrous $CaCl_2$. It was then distilled under reduced pressure before use. Acrylonitrile was separated from stabilizer by washing with 0.1 N KOH followed by distilled water and dried over $CaCl_2$. It was distilled at at-mospheric pressure over P_2O_5 before used. Acrylamide and maleic acid were purified by recrystallization from methanol, while the remaining reagents were used without further purification.

Grafting Procedures

Initial attempts at grafting were carried out on small quantities of fibers (weighing approximately 4500 mg). These fibers were removed from the poly-styrene–acrylonitrile shell and cut at points A and B as indicated in Figure 1. Only the co-irradiation (monomer/solvent present during irradiation) grafting technique was utilized to graft the hollow-fiber membranes, which were removed from the shell. The fibers, each approximately 19 cm in length were weighed in a constant-temperature room at 20°C and at a humidity of around 60%. These fibers, together with various monomer and solvent systems were put in

a glass tube (1.5 cm in diameter and 25 cm in length), lightly sealed with cork before sending for irradiation. The radiation source was ^{60}Co gamma ray irradiation. The ^{60}Co source was supplied by the Australian Nuclear Science and Technology (formerly Australian Atomic Energy Commission) and installed at the University of New South Wales. All grafting reactions were carried out in air, using a radiation dose rate of 0.1 Mrad/h.

After irradiation, grafting reactions were allowed to proceed at room temperature for 24 h. Pure graft copolymers were obtained by washing with suitable solvent in a low-temperature soxhlet extractor for 48 h. The reason for using the low-temperature soxhlet extractor was to minimize the possibility of damaging the hollow-fiber membranes. Care was required to make sure that all the membranes were not bent during the course of reaction, otherwise they would be unsuitable for subsequent application. To obtain the grafting yield, the excess liquid from the washed graft copolymers was drained out, and the membranes were air-dried overnight in a fume cupboard. Drying was completed at vacuum with P_2O_5 for 24 h. These fibers were weighed after being conditioned in the constant-temperature room overnight. The grafting yield in each case was determined by the percentage weight increase based on the initial membrane weight. The conditions of grafting these membranes are reported in Table I.

Both co-irradiation and pre-irradiation grafting techniques were employed for grafting of membranes that were in the shell. Since the shell is subject to attack by benzene and becomes opaque and softens on contact with acrylonitrile, only acrylamide and acrylic acid were used in this case.

To ensure that even amounts of radiation were received by the membranes in the shell, the module was rotated (at 1 rpm) during the course of radiation. Pre-irradiation grafting of these membranes was carried out by adding monomer solution to the irradiated fibers and allowed grafting to proceed for 48 h at 40°C. In the case of co-irradiation grafting, the membranes were soaked overnight in monomer solution, and excess solution was flushed out with nitrogen gas, before irradiation. The reason for doing this was to avoid formation of excessive homopolymer, which is hard or impossible to extract. Instead of extracting the homopolymer using the soxhlet extractor, the grafted membranes obtained were washed by continuously pumping distilled water through the lumens of the hollow-fiber membranes and around the outside of the tube bundle. The excess liquid from the grafted membranes was shaken off before drying

TABLE I

Conditions of Grafting for Membranes Removed from the Polystyrene–Acrylonitrile Shell[a]

Monomer/s (M)	Solvent (S)	M : S ratio	Total dose (Mrad)	Extracting solvent
Styrene	Methanol and trace of CCl₄	1 : 1	1.0	Benzene
Maleic acid	Distilled water	1 : 1	1.0	Distilled water
Acrylamide and maleic acid	Distilled water	12 : 12 : 76	0.025	Distilled water
Acrylonitrile	Methanol	20 : 80	0.025	DMF

[a] All the grafting reactions were done using the co-irradiation grafting technique.

at vacuum with P_2O_5 until constant weight was obtained. The percentage of grafting was determined by the percentage weight increase based on the initial membrane weight.

Again, the preceding reactions were carried out in air and irradiated with a ^{60}Co source at a dose rate of 0.1 Mrad/h. The conditions of grafting of these membranes are summarized in Table II.

Membrane Characterization

The tensile properties of the virgin and grafted membranes were measured using an Instron tensile tester Model 1122 (Universal Testing Instrument). All these measurements were carried out under the following conditions:

Gauge length = 50 mm

Crosshead speed = 10 cm/min

Chart speed = 50 cm/min

Full-scale load = 5 N

The test was carried out on a single hollow-fiber membrane. Ten tests were made on each fiber sample and the average value was reported. Water permeation tests were also carried out on these fibers at a transmembrane pressure of 50 kPa using prefiltered distilled water. For the fibers that were removed from the shell, the same test was carried out by mounting approximately 200 fibers with silicone gel into a 1-cm diameter glass tube with 2 side arms.

RESULTS AND DISCUSSION

The properties of graft copolymers obtained by grafting the hollow-fiber membranes that were removed from the shell as well as those that were still in the shell are given in Tables III and IV respectively. The tensile properties of the modified membranes are reported in terms of their breaking loads and breaking extensions. A typical flux vs. time profile is given in Figure 2.

As can be seen from Table III, only membranes grafted with styrene showed improved physical properties over the virgin membranes as well as possessing higher water flux. The use of styrene grafting of cellulose acetate as a means to improve the mechanical stability of cellulose acetate membranes has been

TABLE II
Conditions of Grafting for Membranes Housed in Polystyrene–Acrylonitrile Shell

Monomer (M)	Solvent (S)	M : S ratio	Total dose (Mrad)	Grafting technique
Acrylamide	Distilled water	1 : 1	3.0	Pre-irradiation
		3 : 7	2.0	Co-irradiation
Acrylic acid	Distilled water	1 : 1	3.0	Pre-irradiation
		3 : 7	2.0	Co-irradiation

TABLE III
Properties of Grafted Membranes (not in the Shell)[a]

Monomer grafted	% grafting	Breaking load (N)	Breaking extension (%)	Steady-state water flux[b] ($1/m^2/h$)
Styrene	96	2.18	33.7	3.0
Maleic acid	5.0	1.25	26.0	2.6
Maleic acid and acrylamide	10	1.80	22.0	0.3
Acrylonitrile	6.6	1.68	32.0	0.8
Unmodified membranes	/	1.93	31.7	1.0
Irradiated membranes (0.025 Mrad)	/	1.60	30.0	0.8
Irradiated membranes (1.0 Mrad)	/	1.41	29.2	0.6

[a] Conditions of grafting for these membranes are given in Table I.

[b] Transmembrane pressure = 50 kPa.

reported.[1,2,3,7] The observed improvement in the tensile properties was probably a result of the presence of the low creep polystyrene. The addition of CCl_4 (Table I), as suggested by Bentvelzen et al.[6] was to promote formation of shorter graft side chains. Bentvelzen et al.[6] used very high CCl_4 monomer ratios, but only trace amounts (0.2%) of CCl_4 was added in this case because large amounts of CCl_4 appeared to weaken the cellulose membranes after irradiation, since CCl_4 is a good chain transfer agent and possibly also promotes degradation of cellulose.

Even with trace amounts of CCl_4 added, the grafted membranes also gave higher water fluxes as compared to the virgin membranes. Similar observations

TABLE IV
Properties of Grafted Membranes (in the Shell)[a]

Monomer grafted	% grafting	Breaking load (N)	Breaking extension (%)	Steady-state water flux[b] ($1/m^2/h$)
Acrylamide				
Pre-irradiation	10	1.53	26.0	0.55
Co-irradiation	20	1.95	25.6	0.62
Acrylic acid				
Pre-irradiation	10	1.70	32.0	0.46
Co-irradiation	23	2.01	23.6	0.64
Virgin membranes	/	1.93	31.7	1.00
Irradiated membranes (2.0 Mrad)	/	1.35	27.2	0.58
Irradiated membranes (3.0 Mrad)	/	1.32	25.6	0.42

[a] Conditions of grafting for these membranes are given in Table II.
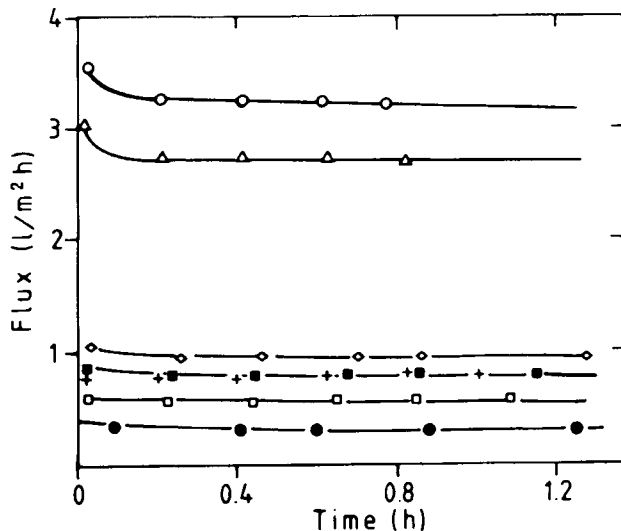
[b] Transmembrane pressure = 50 kPa.

Fig. 2.　Flux vs. time profile. (○) 96% styrene grafted membranes; (△) 5% maleic acid grafted membranes; (◇) unmodified membranes; (■) irradiated membranes (0.025 Mrad); (+) 6.6% acrylonitrile grafted membranes; (□) irradiated membranes (1.0 Mrad); (●) 10% acrylamide and maleic acid grafted membranes. NB: All membranes were grafted using the co-irradiation grafting technique.

were reported by Bentvelzen et al.[6] The increase in water flux can be explained by the fact that the graft chains must have caused an opening effect in the membranes structure. This argument is supported by the work of Arthur[9] who observed layering or opening of the styrene–cellulose graft copolymer.

Membranes grafted with maleic acid gave an overall deterioration in tensile properties. According to Moore,[10] there are cases where grafted fibers showed such behavior, but they normally possess improved surface properties. However, these membranes gave considerably higher water fluxes if one considers the fact that only a small amount of this monomer (5%) was being grafted. The reason for such a low level of grafting was that maleic acid ($COOH-CH_2=CH_2-COOH$) is a monomer that does not undergo homopolymerization (probably due to its bulky end groups).[11] A significant increase in weight of the grafted fibers is not possible (hence the low grafting levels) since the graft side chains obtained are only of single molecule length.[11] These molecules are bulky in nature and each has a specific site of attachment throughout the cellulose backbone; consequently, one would expect an opening effect in the internal structure of the fibers, offering less resistance to the passage of water.

Co-irradiation grafting of acrylamide gave excessive amounts of homopolymer even at low radiation doses (0.025 Mrad). The tendency of acrylamide to homopolymerize rather than attaching itself to the substrate polymer suggested that it has higher G_R value (i.e., number of radicals formed/100 eV) than the cellulose membrane ($G_R = 2.88$).[12] To reduce the overall activity of acrylamide, maleic acid (a monomer that does not polymerize) was added to this grafting solution. After irradiation, the grafting solution became slightly viscous, but pure copolymer was still obtainable by extracting with water. However, the grafted membranes obtained in this way showed poorer tensile properties and

gave lower water fluxes as compared to the virgin membranes. The grafted membranes showed a slight improvement in the breaking load when compared to the irradiated (only) membranes (see Table III for membranes irradiated at 0.025 Mrad). In this comparison, grafting appears to compensate for the loss of strength due to irradiation. The overall deterioration of physical properties of the grafted membranes when compared with the unirradiated membrane was probably due to the action of radiation on cellulose. The presence of polyacrylamide and maleic acid as graft side chains in this case is not sufficient to remedy the damage being done, since these polymers themselves are very water sensitive and do not provide mechanical stability to the substrate polymer. The readiness of acrylamide to polymerize infers an ease of forming long graft chains. These graft side chains probably filled up the void volume in the membrane, making it more resistant to water flow.

Grafting of membranes using acrylonitrile as monomer also gave poorer tensile properties and slightly lower water flux. Like acrylamide, acrylonitrile also has a tendency to homopolymerize very easily. Consequently, the observed water flux decrease in the grafted membranes would probably be due to the partial blockage of the internal membrane structure by the graft side chains. The deterioration of tensile properties of the grafted membranes was probably caused by the action of radiation on cellulose. The presence of graft side chains was probably too little to restore the membranes to their original conditions, even though they showed some improvements over the irradiated (only) membranes (see Table III).

Results obtained for grafting of membranes that are housed in the polystyrene–acrylonitrile shell are summarized in Table IV. Membranes grafted with acrylic acid and acrylamide using the pre-irradiation grafting technique exhibited poorer tensile properties as far as the breaking load of the fibers was concerned. However, these membranes showed a slight improvement in physical and permeation properties when compared with that of the irradiated (only) membranes (comparison made at 3 Mrad, which applied for the grafting using acrylic acid and acrylamide monomers—see Table IV). As explained earlier, the action of radiation on cellulose was probably responsible for the observed physical deterioration while the presence of graft side chains was not able to remedy the damage done.

Co-irradiation grafting of these membranes on the other hand showed improved physical properties but gave lower water permeabilities than those of the virgin membranes. Grafting using this technique required the membranes to be irradiated under swollen conditions. This probably protected the fibers from damage by the full extent of the radiation. Furthermore, the presence of graft side chains probably filled up some of the void volume in the membranes thus adding some physical stability. The filling of these void volumes also explains why lower water fluxes are observed.

Another interesting feature to note from Table IV is that the pre-irradiation grafting technique generally produced membranes with lower water flux than that of the membranes modified using the co-irradiation grafting technique, despite the fact that a higher percentage of grafting was observed in the latter case. Recently, Takesawa et al.[13] examined the effects of gamma radiation on the structure of cellulosic dialysis membranes and found that the molecular weight cutoff of the membranes decreased if the membranes were irradiated

under dry conditions, while the reverse was true for membranes irradiated under wet conditions. The pre-irradiation grafting technique used in this work requires the membranes to be irradiated under dry conditions, thus the observed reduction in water permeability could be anticipated from Takesawa's et al. results.[13] Membranes grafted using the co-irradiation grafting technique were irradiated under swollen conditions, so higher fluxes could be expected despite the higher percentage of grafting obtained. However, unlike the results reported by Takesawa et al.,[13] the co-irradiation grafting does not always produce membranes with higher water flux. As explained earlier, this may be due to the nature of the graft side chains present.

CONCLUSIONS

Radiation-induced grafting can be done successfully on regenerated hollow-fiber membranes. The type of monomer used can influence the permeation properties of the modified membranes. Membranes that are easily homopolymerizable (i.e., those with high G_R value) tend to produce membranes with lower permeability. The choice of grafting technique (i.e., pre-irradiation or co-irradiation) also influences the permeation property. For the same type of monomer, co-irradiation grafting generally produces membranes with higher permeability than that of pre-irradiation grafting.

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