

Studies on Structural Transformation of the Styrene-Grafted Polyethylene Film and Fabric — Grafting Behavior and Cavity Formation Mechanism

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Synopsis

A new approach to prepare hydrophilic porous membranes is presented. Films and fabric made of polyethylene were grafted with styrene by simultaneous γ -irradiation. The grafting behaviors of fabric are quite different from bulk films which exhibit the well-known gel effect in styrene-methanol mixture solutions. The grafting rate for fabric increased monotonically with monomer concentration, and no maximum appeared on dilution with methanol. The copolymer films were further sulfonated to prepare hydrophilic membranes. Surface structure of membranes and fabrics were examined with optical and electron microscopy. For the fabric, the original smooth surface turned into rugged surface with different sizes of cavities. For membranes, the buldgelike bubbles are found when swollen with water. These bubbles changed into cavities after drying in vacuum at elevated temperature. The mechanism for the formation of such a structure is discussed. The electrical resistance of such membrane was low enough to be useful as battery separator.

INTRODUCTION

Graft polymerization has long been used to modify the properties of polymers due to its superiority to conventional physical or chemical methods. Structural changes after graft polymerization of styrene onto polyethylene films have been studied.¹⁻⁵ However, structural changes on grafted polyethylene fabric and membranes after extraction and sulfonation have not been studied so far.

In view of utilization of radiation-induced graft polymerization for modification of polymer surface structure, polyethylene films, and fabric were grafted with styrene by gamma radiation. This article reports the differences in grafting behaviors of polyethylene film and fabric. These materials were characterized after extraction and sulfonation by optical and scanning electron microscopy. The areal resistance of the membrane was measured to evaluate their use as separators of high performance lead-acid battery.

EXPERIMENTAL

Materials

Polymers

The materials used as grafting substrate included: (1) high-density polyethylene film (HDPE) with density 0.953 g/cm³, melt index 3.0 g/10 min

and thickness 0.020 mm, (2) low-density polyethylene film (LDPE) with density 0.921 g/cm³, melt index 3.0 g/10 min and thickness 0.120 mm, (3) blended polyethylene film (abbreviated as MDPE), equal part of LDPE and HDPE were blended together, thickness 0.030 mm (these films were kindly supplied by USI Far East Corp), and (4) polyethylene fabric, from NCB Industries Co. Japan, is woven of 50 denier monofilament into screen structure, density of fabric 156 × 100 (in in. unit), thickness of the woven fabric is 0.20 mm.

Films or woven fabric were washed with acetone, immersed in *n*-hexane for 48 h, dried under vacuum at 50°C for 24 h, and then stored in a vacuum oven at room temperature before grafting.

Monomers

Styrene was freed of inhibitor by washing three times with 10% sodium hydroxide solution and then with water until the washings were neutral, the monomer was dried over sodium carbonate and magnesium sulfate, and then distilled under reduced pressure before use.

Reagents

Reagent grade sulfuric acid (95% min) and silver sulfate (99.5% min) were used in the sulfonation process. Reagent grade methanol was used as diluent in the graft polymerization and industrial grade toluene was used to extract any free polystyrene.

DSC Measurement

DSC measurement was made by using a Perkin-Elmer Model DSC-2 at a heating rate of 10 K/min to 430 K. Several layers of samples were pressed in the sample cup to a reasonable weight. The instrument was calibrated with indium. The heat of melting of completely crystalline polyethylene was taken as 68.4 cal/g.⁶ Crystallinity was calculated by weighing the chart paper to determine the area under the thermogram curve.

Grafting Procedure

Weighed polyethylene immersed in monomer solution were enclosed in an envelope made of polyethylene. Irradiation was performed with cobalt-60 gamma ray of dose rate 0.187 Mrad/h. The temperature of the experiments was 20°C.

In mutual γ -radiation-induced grafting polymerization a simple technique in which the solution was not deoxygenated have been studied.^{7,8} Although oxygen inhibit the polymerization until it is consumed by radicals produced by the radiation. In view of practical application, solutions were used without further deoxygenation.

For our purpose this is sufficient because only small amounts of oxygen, if any, may diffuse from the monomer solution into the polyethylene matrix and the dose rate is high enough to reduce its effect.

Scanning Electron Microscopy

A JEOL JXA-50A scanning electron microscope (SEM) was used. The samples were coated with sputtered films of gold/palladium alloy.

Extraction and Sulfonation

After radiation the grafted copolymer films and fabric were removed and washed with toluene, and then immersed in toluene at 50°C for 48 h to extract homopolystyrene. The samples were dried under reduced pressure at 60°C for 24 h.

The degree of grafting was obtained from the weight increase of the films according to the following equation

$$\% \text{ graft} = \frac{w_1 - w_0}{w_0} \times 100\%$$

where w_0 is the initial weight of the substrate and w_1 is the weight of grafted copolymer. The polyethylene-*g*-styrene copolymer films were sulfonated with concd sulfuric acid containing 1% silver sulfate at 50°C for 24 h.

Electrical Resistance

The electrical resistance of the sulfonic acid type membranes were measured in the sulfuric acid of specific gravity 1.240 at 25°C using an Ohmmeter (LCR meter ZM-341, NF Electrical Instruments) working at 1000 Hz.

Samples after soaking for 24 h in sulfuric acid of sp. gr. 1.240 were clamped between two platinized platinum electrodes. The test cell was designed such that the area of the exposed surface was approximately 1 cm².

RESULTS AND DISCUSSION

Grafting Behavior

Grafting behavior of styrene onto LDPE is shown in Figure 1. It is clear that a higher grafting rate appeared at 30 vol % styrene in each of the irradiation intervals. The acceleration effect by adding methanol has been observed, and the explanation was offered in terms of the monomer concentration and viscosity of the amorphous region of polyethylene.⁹

Moreover, in our experiment 3 h of irradiation always gave the maximum grafting rate with monomer concentration between 30 and 70 vol % styrene. Besides the effect of methanol, we also attribute this to the following two effects.

1. Oxygen dissolved in the solution inhibited the polymerization initially until they were consumed by the free radicals produced by irradiation. Therefore, the polymerization rate rises as oxygen is consumed.

2. Change of composition of matrix and outside solution as the reaction continues. The matrix and outside solution are becoming polystyrene-rich

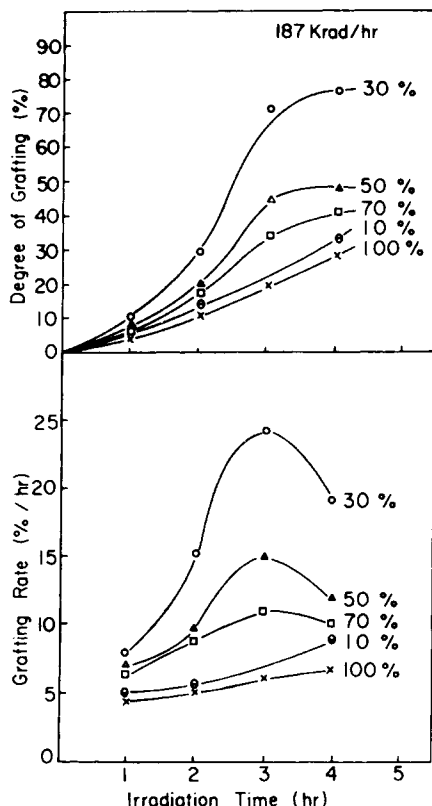


Fig. 1. Degree of grafting vs. irradiation time (upper) and grafting rate vs. irradiation time (lower) at 20°C, 187 krad/h in LDPE-methanol-styrene system (vol % of styrene): (X) 100; (□) 70; (△) 50; (○) 30; (⊖) 10.

leading to lower monomer concentration in the outside solution. The initial grafted polystyrene was found to enhance the solubility of styrene.¹⁰ This will facilitate the graft polymerization reaching the maximum grafting rate at 3 h of irradiation and decreases further radiation because of monomer consumption.

The grafting behavior of HDPE is shown in Figure 2 a slight difference in grafting curve from that of LDPE may be ascribed to the crystallinity and thickness of the matrix which would affect the absorption of monomer and radical production.

Here the effect of monomer concentration on the grafting yield is more complicated. The maximum grafting yield within 2 h of radiation was in concentration of 70 vol % styrene for HDPE whereas it was 30 vol % for LDPE. But on further irradiation, solution with lower initial monomer concn produced higher grafting yield. The acceleration effect in 30 vol % again appeared. This grafting behavior may be explained in terms of increasing solubility of styrene initially as styrene is being grafted and of decreasing diffusion gradually due to homopolymerization.

The grafting behavior of polyethylene fabric at various styrene/methanol compositions is shown in Figure 3. As the concentration of methanol increases, the degree of grafting decreases. Acceleration effect was not found

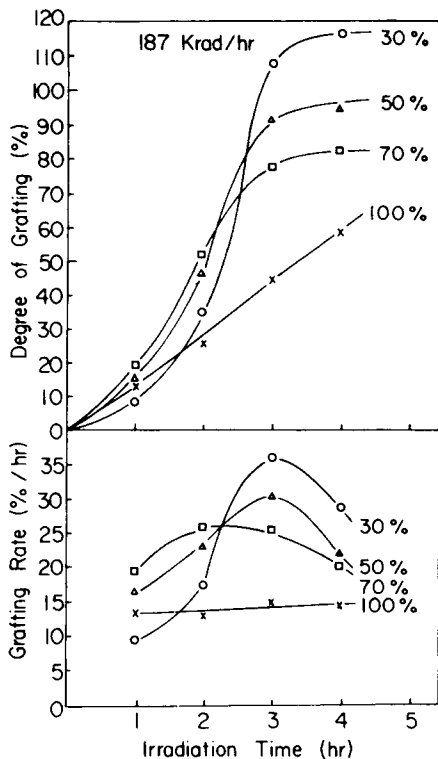


Fig. 2. Degree of grafting vs. irradiation time (upper) and grafting rate vs. irradiation time (lower) at 20°C, 187 krad/h in HDPE-methanol-styrene system (vol % of styrene): (X) 100; (□) 70; (△) 50; (○) 30.

on addition of methanol. The degree of grafting increases with monomer concentration. But the grafting rates are much less than that of bulk film. A separate experiment had been made on MDPE and polyethylene fabric immersed together in the same 30 vol % styrene solution, and it was found that the degree of grafting is 75% for MDPE compared to 2% for fabric after 3 h of irradiation.

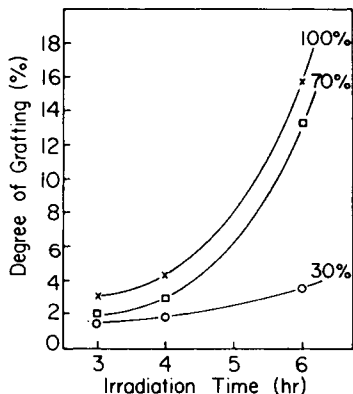


Fig. 3. The effect of methanol on the grafting of PE fabric immersed in O₂ containing styrene-methanol solution, dose rate 187 krad/h at 20°C; styrene (vol %) (X) 100; (□) 70; (○) 30.

From DSC measurement, the crystallinity of the polyethylene fabric was calculated to be 78 ± 2 wt %, which is higher than that of HDPE whose crystallinity is 67 ± 2 wt %. Also the diameter of each fiber is larger than the thickness of the HDPE bulk film. Furthermore, it has been found that the diffusivity of styrene decreases with the increasing degree of grafting for HDPE, and the decrease begins at quite a low degree of grafting.¹¹ This also supports our finding that the grafting rate for fabric is less than that for bulk film.

Electron Microscopy Observation

Structure of Polyethylene Fabric

Figure 4 shows the scanning electron micrographs of the polyethylene fabric before and after grafting. It is clear that the surface of each fiber is very smooth originally. After radiation-induced grafting polymerization it is smooth too, but, when the sample was further extracted with hot toluene, large circles appeared at the curved site of each fiber. A larger number of smaller circles could be seen between the large circles on magnification. On close examination of the micrographs these circles appeared to be cavities, and this structure is believed to form and grow during the soaking of the fabric in toluene.

Also, fibrillar structure can be seen in the circles. From the grafting behavior and cavity structure, it may be confirmed that diffusion of monomer is retarded and grafting polymerization occurs only at certain sites. Explanation will be given by the following.

In the production of the fabric, drawing and weaving exerted force on the fiber; thus the amorphous regions are torn under loading along the axis of orientation, leading to the formation of submicrocracks.¹² Furthermore, the interfibrillar holes may also be formed due to mutual slippage of fibrils.¹³ Thus the monomer will preferentially occupy the holes or microcracks near the upper surface and will polymerize there or produce grafted chains at the surface of the lamellae¹⁴ surrounding the microcracks.

It has been presumed that pressure exerted by expanding regions, primarily due to the homopolystyrene, is sufficient to break the loose, lateral intercrystalline links.^{5,3} Such an effect may facilitate the diffusion of styrene into these intercrystalline regions. But the diffusion of monomer deep into the matrix will be hindered more than the peripheral diffusion; thus polymerization will proceed from the microcracks and expand the polystyrene domain radially.

Beside homopolystyrene which are easily removed from the near surface, some quantity of grafted lower molecular weight polyethylene chains are also soluble in toluene. These macromolecules will dissolve away and leave behind a cavity structure.

Structure of the Bulk Film

The formation of bubbles in the radiation-induced grafting of styrene to polyethylene by the simultaneous irradiation method has been reported.^{1,15-17} Such a bubble structure has long been thought of as a shortcoming

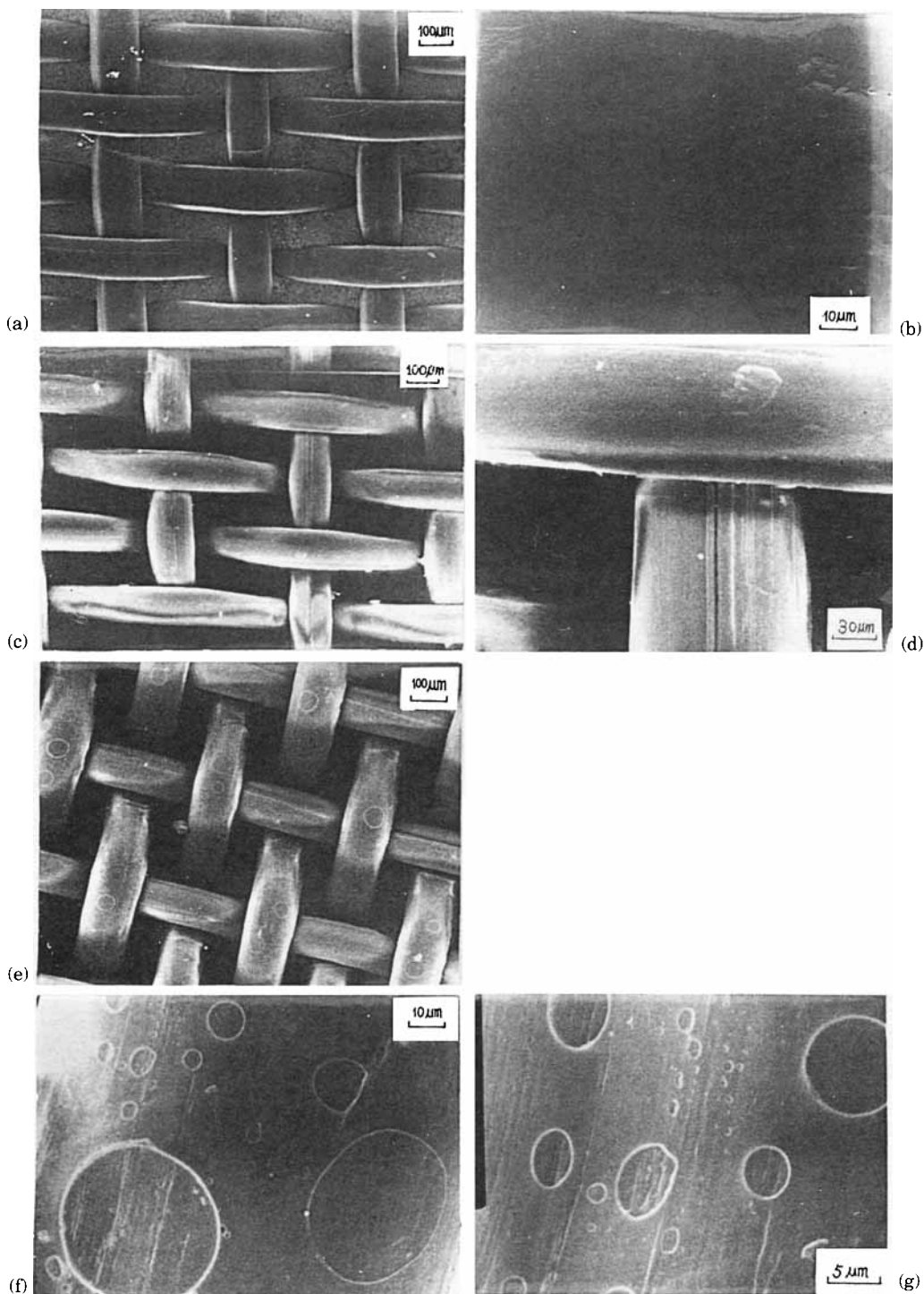


Fig. 4. Photomicrographs of the polyethylene fabric: (a,b) surface on original fabric; (c,d) after radiation for 6 h in pure styrene; (e,f,g) after radiation grafting and extraction procedure; (f and g) fabric surface on magnification showing the cavity structure.

due to the homopolymer and was of no use in view of practical application. But we can successfully transform such a bubble into a cavity structure, and use this as a new approach to prepare porous hydrophilic separator for electrochemical cells.

Our preliminary result on the formation of cavity is shown in Figure 5. The cavity structure is believed to result from the collapsing of the bubble produced by the penetration of the occluded macromolecules, primary of polystyrene or its sulfonic derivatives.

Similarly, a white circular structure could be observed having a dimension close to that of fabric appearing at the curved site. This may be ascribed to the homopolystyrene too.

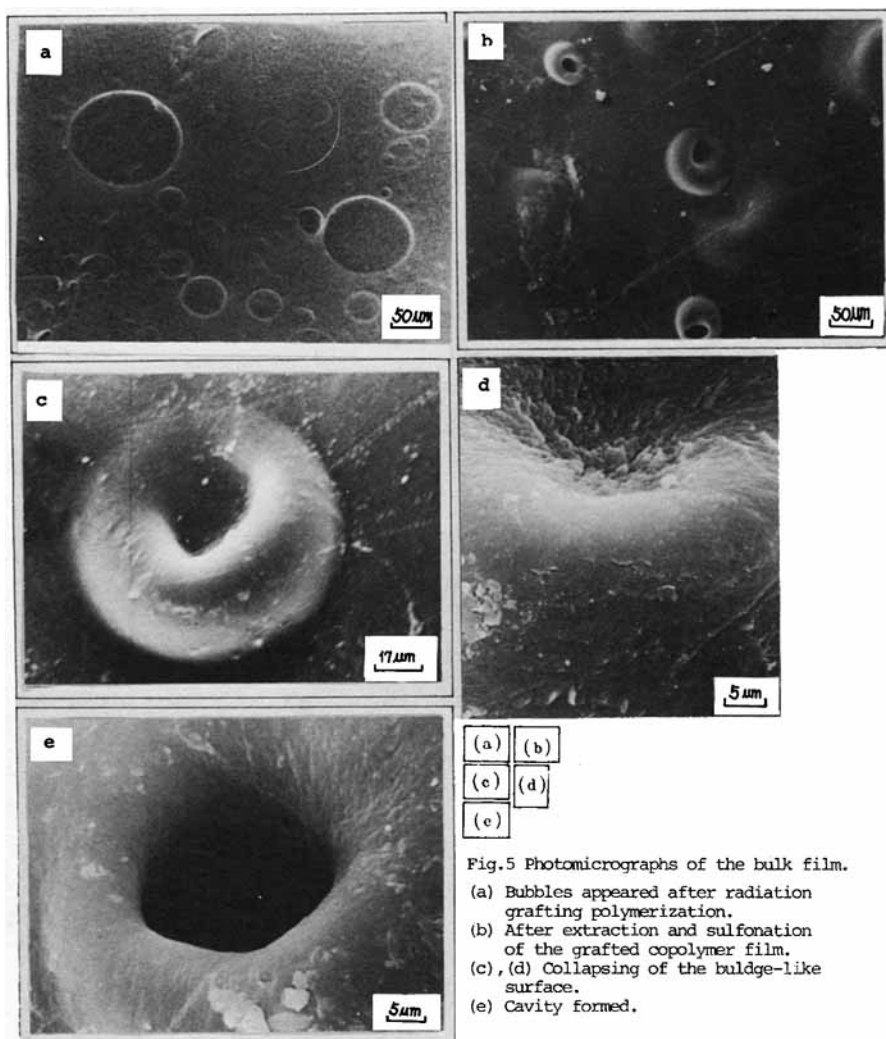


Fig.5 Photomicrographs of the bulk film.

- (a) Bubbles appeared after radiation grafting polymerization.
 (b) After extraction and sulfonation of the grafted copolymer film.
 (c),(d) Collapsing of the buldge-like surface.
 (e) Cavity formed.

Fig. 5. Photomicrographs of the bulk film: (a) bubbles appeared after radiation grafting polymerization; (b) after extraction and sulfonation of the grafted copolymer film; (c,d) collapsing of the buldge-like surface; (e) cavity formed.

The photomicrographs clearly showed the collapsing of bubbles and finally forming cavity of 50 μm diameter. Formation of such a structure was proposed to proceed through the following steps.

1. Formation of separate polystyrene domain on irradiation.
2. Bubble formation while soaking in toluene.
3. Protruding of the surface owing to the swelling pressure of polystyrene sulfonic acid, which may swell greater in aqueous solution.
4. Pressure difference between the inner side of the bubbles and outer atmosphere when the swelling bubbles are dried under vacuum oven at elevated temperature. The inner expanding pressure would finally break the bubble surface and collapse of the bubbles leading to the formation of cavity structure.

Several workers on the analysis of apparent graft and true graft are summarized in Table I. In our study, the degree of grafting refers to apparent graft. That is, the trapped homopolystyrene are not completely separated for preserving the integrity of the bulk film. As one can see in the eighth column, the fraction of true grafting in overall polystyrene depends upon grafting conditions which are shown in the same table.

Kamel¹⁸ ascribed the higher covalent graft yield of 0.73 to lower monomer concentration which would reduce the homopolymer initiation rate, while the initiation of grafted chains is unaffected. Thus the homopolymerization rate should be proportional to the square root of monomer concentration.

But the result obtained by Ungar³ was the opposite. He ascribed the large amount of homopolystyrene on the addition of methanol as due to the increase in the initiation for homopolymerization of styrene. This has also been verified.^{19,20} Further it was explained that, as styrene is being consumed, the methanol-to-styrene ratio inside the film increases.³ Work on the solubility of benzene in polyethylene-styrene graft copolymers has been performed, and they concluded that a 50–90% increase in benzene solubility in a 26% graft copolymer film compared to the original polyethylene.¹⁰

It will be reasonable to predict that styrene will exhibit similar behavior to benzene in solubility because they are similar in solubility and viscosity characteristics. [The Hildebrand solubility parameter for benzene and styrene are 9.2 and 9.3 (cal/cc)^{1/2}, respectively, and the viscosity of benzene is 0.564 cP at 30°C, that of styrene is 0.587 cP at 37.8°C.^{21,22}] Therefore, the methanol to styrene ratio inside the film may be simultaneously effected by the increasing solubility.

We attribute the findings of Kamel and Ungar to the fact that low density and high density polyethylene were used, respectively, in their studies. Besides, the dose rate, irradiation hours, and the separation procedure after dissolving in xylene may well affect the amount of homopolystyrene too. These have yet to be studied.

It may be noted that Soxhlet extraction with benzene cannot effectively remove the homopolystyrene. So the values in the parentheses are overestimated. But these data are helpful in confirming our experiment that a considerable amount of homopolymer is still trapped after soaking in toluene. This could be sulfonized to produce polyelectrolyte.

Moreover, it must be stressed that the true graft percentage is always below 40% if the apparent graft did not exceed 100%. Particularly, Chen²⁵

TABLE I
Homopolymer Content and Fraction of True Grafting at Various Conditions^a

Substrate (thickness,mm)	Monomer concentration	Dose rate (rad/h)	Irradiation (h)	Apparent ^b graft percent	True ^c graft percent	Fraction of true grafting in overall PS content	Ratio of homopolystyrene to original film	Ref. no. (author)
LDPE (0.07)	Pure styrene	7.4×10^4	24	99	22.7	0.23	0.76	23
HDPE (0.07)	Pure styrene	7.4×10^4	24	133	47	0.35	0.86	(Matsuda et al.)
LDPE (0.066)	Pure styrene	10^5	5	51	15.1	0.30	0.36	1
	Pure styrene	10^4	5.87	30	14.6	0.49	0.15	(Machi)
LDPE (0.063)	30 vol% styrene in methanol	2.3×10^5	1-5	Up to 200	Up to 400	Average 0.73	—	18
HDPE (0.1)	1:2 styrene to methanol		10	190	50	0.26	1.40	3
	1:2 styrene to methanol	8.6×10^3	21	420	60	0.15	3.60	(Ungar)
HDPE (thickness, not indicated)	Pure styrene		62.5	180	61	0.34	1.20	
	Pure styrene	1.4×10^5	17.5	82.1	(50) ^d	(0.61) ^d	—	24
	Pure styrene		6.87	40.9	(34.3)	(0.84)	—	(Toi et al.)
	Pure styrene		6.04	19.7	(17.9)	(0.9)	—	
	Pure styrene		4.11	10	(9)	(0.9)	—	

^a Some of the data are calculated from references shown in the last column.

^b (mg PS/mg PE) \times 100%, refers to weight increment due to grafting

^c (mg PS/mg PE) \times 100%, refers to covalent grafts PS, homo-PS separated by dissolving in xylene.

^d Values in parenthesis are after Soxhlet extraction, homo-PS may not completely be removed.

TABLE II
Electrical Resistance of the Grafted Copolymer Membrane

Original film LDPE	Apparent graft percent	Areal resistance ($m\Omega\text{ cm}^2$) ^a
No. 1	74	79
No. 2	70	80
No. 3	83	256
No. 4	103	51

^a Measured in sulfuric acid of sp. gr. 1.240 at 25°C.

has found that membranes that contained 20–35% styrene exhibited an optimum combination of mechanical and electrochemical properties. So it would be feasible through a grafting – extraction – sulfonation process to prepare porous hydrophilic membrane separators.

The areal electrical resistance for some of the grafted copolymer membranes is shown in Table II. The resistance was measured in sulfuric acid of sp. gr. 1.240 to evaluate its function as a battery separator. A small amount of sulfuric acid and divinylbenzene was added to increase the apparent graft yield and mechanical property. A higher resistance for sample no. 3 was found to be the result of nonuniform sulfonation through the matrix. The results have shown promise for battery application.

CONCLUSIONS

1. The grafting behavior of polyethylene fabric and bulk film are found to be dependent on both crystallinity and thickness. Different grafting behaviors for polyethylene bulk film and fabric are found and discussed.

2. Direct observation of cavity structure on polyethylene fabric clearly showed the formation of cavity after extraction procedure. Homopolystyrene trapped in microcracks and grafted chains on lower molecular weight polyethylene chains are responsible for the formation of such a structure.

3. The surface of the bulk film changed through bubbles to form large cavity. This transformation resulted from the extraction and sulfonation of polystyrene and subsequent drying under vacuum. A mechanism is proposed for the formation of cavity and confirmed by direct observation with electron microscopy.

4. Electrical resistance of the grafted copolymer membranes showed the possibility of developing a battery separator through the grafting–extraction–sulfonation process.

References

1. S. Machi and J. Silverman, *J. Polym. Sci., A-1*, **7**, 2737 (1969).
2. J. Dobo, *Radiat. Phys. Chem.*, **14**, 863 (1979).
3. G. Ungar, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2137 (1979).
4. G. Ungar and J. Dlugosz, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2151 (1979).
5. I. Smit and A. Bezjak, *Polymer*, **22**, 590 (1981).
6. B. Wunderlich, *Macromolecular Physics*, Academic, New York, vol. 11, pp. 388.
7. J. L. Garnett and N. T. Yen, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 225 (1974).
8. D. M. Pinkerton and R. H. Stacewicz, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 287 (1976).

9. S. Machi, I. Kamel, and J. Silverman, *J. Polym. Sci., A-1*, **8**, 3329 (1970).
10. M. Fels and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 537 (1970).
11. G. Odian, R. Henry, R. Koenig, D. Mangaraj, D. Trung, B. Chao, and A. Derman, *J. Polym. Sci.*, **13**, 623 (1975).
12. V. S. Kuksenko, M. A. Gezalov, A. I. Slutsker, A. A. Yastrebinsky, and V. A. Zakrevsky, *J. Polym. Sci.*, **C38**, 357 (1972).
13. J. Steidl and Z. Pelzbauer, *J. Polym. Sci.* **C38**, 345 (1972).
14. T. Takamatsu, T. Konaga, and E. Fukada, *Chem. High Polym. Jpn.*, **24**, 795 (1967).
15. A. S. Hoffman, E. R. Gilliland, E. W. Merrill, and W. H. Stockmayer, *J. Polym. Sci.*, **34**, 461 (1959).
16. D. Ballantine, A. Glines, G. Adler, and D. J. Metz, *J. Polym. Sci.*, **34**, 419 (1959).
17. D. Ballantine, D. J. Metz, J. Gand, and G. Adder, *J. Appl. Polym. Sci.*, **1**, 371 (1959).
18. I. Kamel, R. P. Kusy, and R. D. Corneliussen *Macromolecules*, **6**, 53 (1973).
19. A. Chapiro, *Radiation Chemistry of Polymer Systems*, Wiley-Interscience, New York, 1962.
20. S. Dilli and J. L. Garnett, *J. Appl. Polym. Sci.*, **11**, 859 (1967).
21. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York, 1975, pp. IV-341, VII-25.
22. Shell Development Co., Technical Data Bulletin, Sc. 61-154.
23. T. Matsuda, K. Hagakawa, B. Eda, and K. Kawase, *Chem. High Polym. Jpn.*, **18**, 634 (1961).
24. K. Toi, M. Kikuchi, and T. Tokuda, *J. Appl. Polym. Sci.*, **21**, 535 (1977).
25. W. K. W. Chen, R. B. Mesrobian, D. S. Ballantine, D. J. Metz, and A. Glines, *J. Polym. Sci.*, **23**, 903 (1957).

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