

Preparation of Hydrophilic Polyethylene Foam of Open Cell Type by Radiation Grafting of Acrylic Acid

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Synopsis

Hydrophilic polyethylene foam was synthesized by radiation grafting of acrylic acid onto polyethylene foam of open cell type using monomer solution containing Mohr's salt which inhibits homopolymerization of the monomer. The graft foam was easily dyed by cationic dyes and showed excellent moisture regain. The wicking properties were also excellent and were almost the same as those of commercially available PVA foam. The surface resistivity of 10^{16} ohm of the original foam decreased to 10^6 ohm and half decay time of surface charge decreased from 8000 s to 1 s by the grafting, indicating that the grafted foam has excellent antistatic properties.

INTRODUCTION

Polyethylene foam of open cell type is superior in hydrophobic character, chemical resistivity, and weather proofness to other foams of open cell type such as polyurethane, and therefore, the open cell-type polyethylene foam is used widely as sealing, heat-insulating, and sound-insulating materials in the electric, civil, and construction industries. By modifying the polyethylene foam of open cell type to give hydrophilic properties, the foam will find uses additional to those mentioned above. For this purpose, the present study has been carried out on the radiation-induced grafting of acrylic acid to the foam. No radiation grafting to the synthetic polymer materials in foam form has been reported as far as we know. Air, which accounts for most of the volume of the foam material, is considered to inhibit radiation-induced grafting; this was confirmed by our preliminary study using a well-established conventional technique¹ in which the air was removed from monomer solution by bubbling nitrogen before the grafting. By further removal of air from cells in the foam and impregnation of nitrogen-saturated monomer solution, we proceeded successfully to induce grafting.

The high rate of polymerization of acrylic acid lends great advantage to use of this monomer for its high rate of grafting, but has a disadvantage in that a large amount of unwanted homopolymer is produced in the monomer solution. One of the present authors studied the effect of various inhibitors on the radiation grafting of acrylic acid onto polyester fiber² and found that addition of ferrous ion or cupric ion resulted in smooth grafting without producing

homopolymer in the monomer solution. Among the metal salts studied, Mohr's salt(ferrous ammonium sulfate) gave the most suitable results.

It is true that in the preirradiation method, smooth polymerization is possible without any inhibitors by selecting appropriate reaction conditions, but the addition of inhibitor to the monomer solution seems preferable for further industrial purposes, because complete prohibition of homopolymer formation in the monomer solution will allow repeated use of the monomer solution and also easy handling of the grafted products. For the reasons mentioned above, we selected acrylic acid solution containing Mohr's salt as inhibitor. In this article we report the grafting behavior of acrylic acid onto open cell type polyethylene foam by preirradiation method and also report hydrophilic properties of grafted foam thus obtained.

EXPERIMENTAL

Materials

The open cell type polyethylene foam was supplied by Sanwa Kako Co. (type LC-300 #2, thickness, 0.5 cm; apparent density, 0.0288 g/cm³; average radius of cell, 1 mm). Acrylic acid (AA) of extra-pure grade containing 200–500 ppm hydroquinone monomethyl ether as stabilizer was purchased from Nakarai Chemicals Co. and was used as received. Mohr's salt used as inhibitor was also supplied by Nakarai Chemicals Co., and was of guaranteed reagent grade.

Preparation of the Monomer Solution

Stock solution containing 8×10^{-3} mol/L Mohr's salt was prepared from distilled water in a 1 L volumetric flask. The stock solution was diluted to a desired concentration of Mohr's salt and then acrylic acid was added to the solution for use as monomer solution.

Preirradiation

The foam, cut to an appropriate size, was sealed in a polyethylene bag in nitrogen atmosphere, and then irradiated with electronic beam (1.5 MeV and 50 μ A) from a Van de Graaff accelerator, at dose rate of 1.75×10^5 rad/s.

Grafting Procedure

After irradiation, the foam was transferred to a reaction vessel containing monomer solution without exposing to air and was impregnated with monomer solution by repeated cycles of mechanical compression and expansion in nitrogen atmosphere. The reaction vessel was warmed for grafting in a water bath kept at 35°C for the desired reaction time. After grafting, the foam was removed from the reaction vessel, washed with running water, and further dipped in 50°C water for more than 6 h to remove homopolymer. During extraction in 50°C water, the samples were squeezed several times to remove the homopolymer completely. The grafted foam was then dried in a vacuum oven for constant weight and the graft percent was calculated from the weight increase after the grafting procedure.

No experimental data were obtained for the grafted foam prepared at zero % salt, since it was impossible to separate grafted foam from homopolymer, which firmly adhered to the foam surface.

Conversion of PAA Graft Chain to Sodium Salt

The foam grafted with acrylic acid was immersed in 1% aqueous solution of sodium bicarbonate for 2 h at 80°C to convert PAA graft chain to sodium salt.

Properties of Acrylic Acid-Grafted Foam

Hydrophilic properties such as dyeability, hygroscopicity, antistatic property and wicking behavior, and tensile property of the acrylic acid-grafted foam were examined. The method of evaluation of each property will be described in the Results section.

RESULTS AND DISCUSSION

Grafting Reaction

Time conversion curves and effect of Mohr's salt added in the system. In Figure 1, the graft percent is plotted as a function of reaction time for the monomer solutions (AA : H₂O = 50 : 50 and 95 : 5 by vol) containing different amounts of Mohr's salt and acrylic acid at 35°C and at preirradiation dose of 5 Mrad. At any concentration of Mohr's salt and acrylic acid, the graft percent increased rapidly at the early stage of the reaction and reached

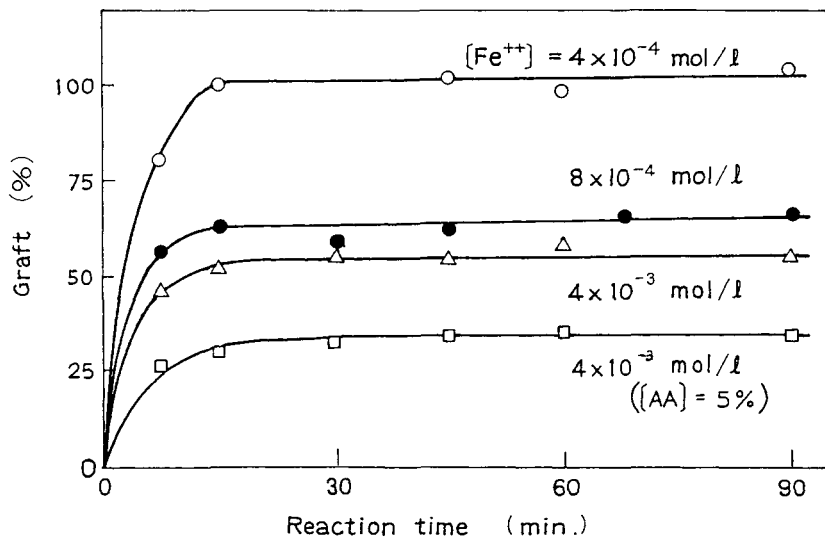


Fig. 1. Grafting of acrylic acid onto polyethylene foam at different concentrations of Mohr's salt; (○) 4×10^{-4} mol/L, (●) 8×10^{-4} mol/L, (Δ) 4×10^{-3} mol/L; Preirradiation dose: 5 Mrad; concentration of AA: 50% by volume; Reaction temperature: 35°C; The time conversion curve obtained for the monomer solution containing 5% AA and 4×10^{-3} mol/L Fe^{2+} is indicated by (□).

plateau values, which are referred to as final graft percent (FGP). As shown in the figure, the initial increase of conversion is too high to allow precise determination of initial rate of grafting but it is still apparent enough to confirm that the higher the initial rate of grafting, the higher the FGP obtained.

FGP depends on the concentrations of both Mohr's salt and acrylic acid in the monomer solution; higher FGP was obtained with lower Mohr's salt concentrations, and also by higher concentrations of acrylic acid if the Mohr's salt concentrations are the same. It is noted that graft percent reached near plateau value of 30% in 15 min at acrylic acid concentration as low as 5%.

The final graft percent is plotted as a function of Mohr's salt concentration in Figure 2, where it is evident that the graft percent depends on the concentration of Mohr's salt at high monomer concentration: at monomer concentration of 50%, FGP decreased from 100% to 60% with increasing concentration of Mohr's salt from 4×10^{-3} mol/L to 8×10^{-3} mol/L. But further increase of Mohr's salt concentration resulted in a slight decrease of FGP. It is also clear from the figure that as the monomer concentration decreases, the effect of Mohr's salt concentration on FGP lessens, and at 5% monomer concentration, only 5% decrease of FGP was observed with increase of Mohr's salt concentration by an order of magnitude from 4×10^{-4} mol/L.

Effect of monomer concentration on FGP. Figure 3 shows the effect of monomer concentration on FGP. At 10^{-4} mol/L, concentration of Mohr's salt, the FGP increases linearly with increasing monomer concentration in the range between 5 and 50%, while at 10^{-3} mol/L Mohr's salt concentration, FGP does not increase linearly, but the slope becomes less sharp as the monomer concentration increases. The reason for this may be that Mohr's salt prohibits some grafting of acrylic acid.

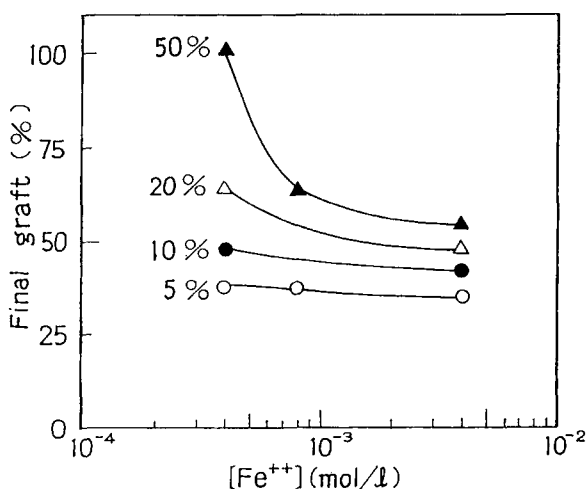


Fig. 2. Final graft percent as a function of Mohr's salt concentration at different monomer concentrations; Concentration of AA (by vol); (○) 5%, (●) 10%, (△) 20%, (▲) 50%; Preirradiation dose: 5 Mrad; Reaction temperature: 35°C.

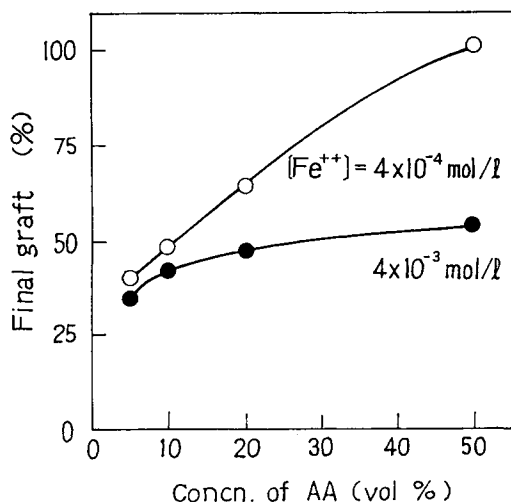


Fig. 3. Final graft percent as a function of monomer concentrations; Preirradiation dose: 5 Mrad; Concentration of Mohr's salt: (○) 4×10^{-4} mol/L, (●) 4×10^{-3} mol/L; reaction temperature: 35°C.

Effect of preirradiation dose on FGP. In Figure 4, FGP is plotted as a function of preirradiation dose. FGP increased with increasing dose up to 5 Mrad, but the increment of FGP with increasing dose became smaller above 5 Mrad. The radicals are built up in the crystalline region of polyethylene during irradiation. These radicals migrate out from where they were originally trapped to the surface of the crystallites and then undergo the grafting reaction with monomers competing with recombination reaction between radicals. Thus, the higher the dose, the higher the concentration of the released radicals on the crystallite surface, resulting in inefficient consumption

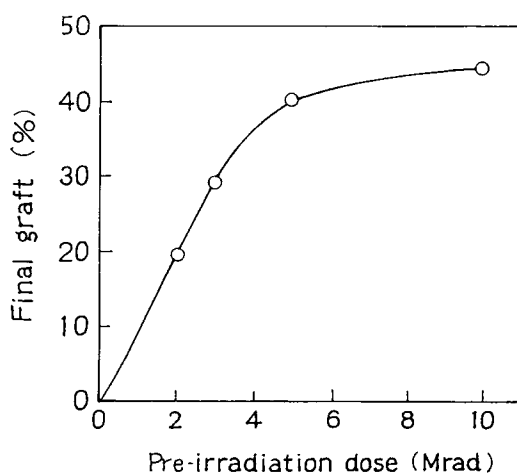


Fig. 4. Final graft percent as a function of preirradiation dose; Concentration of acrylic acid in monomer solution: 5% (by vol). Concentration of Mohr's salt: 4×10^{-4} mol/L; Reaction temperature: 35°C.

of radicals for the grafting. This may account for the observed small increment of FGP with dose above 5 Mrad.

Properties of Acrylic Acid Grafted Polyethylene Foam

Dyeability

The original polyethylene foam cannot be dyed at all, but it becomes dyeable with cationic dyes when carboxylic groups are introduced to polyethylene chains. Homogeneous but poor dyeability was obtained by 2% grafting when the grafted foam was dyed with Sevron Brilliant Red B by the method mentioned in the former report,³ but for satisfactory deep dyeability, grafting of more than 20% graft percent was necessary.

Hygroscopicity

In Figure 5, moisture regain of the grafted foam is plotted as a function of graft percent when the grafted foam was equilibrated with moisture at 66% and 93% relative humidities. The broken line indicates the moisture regain calculated from the graft percent provided that the moisture regain of the grafted foam be equal to the sum of the value of each component multiplied by weight fraction of the component. In the atmosphere of low relative humidity (at 66%), the observed moisture regain of the grafted foam agreed well with the calculated value, but at high relative humidity, the observed value was lower than the calculated one in the whole range of graft percent. The result means that at low relative humidity, the complete equilibrium of moisture exists between foam and atmosphere, but at high relative humidity, some entanglement of polyethylene chains and polyacrylic acid (PAA) chains may restrict the movement of chain segments of the latter to inhibit hydration of some fraction of carboxylic groups in the PAA chains, thus giving lower moisture regain than the calculated value.

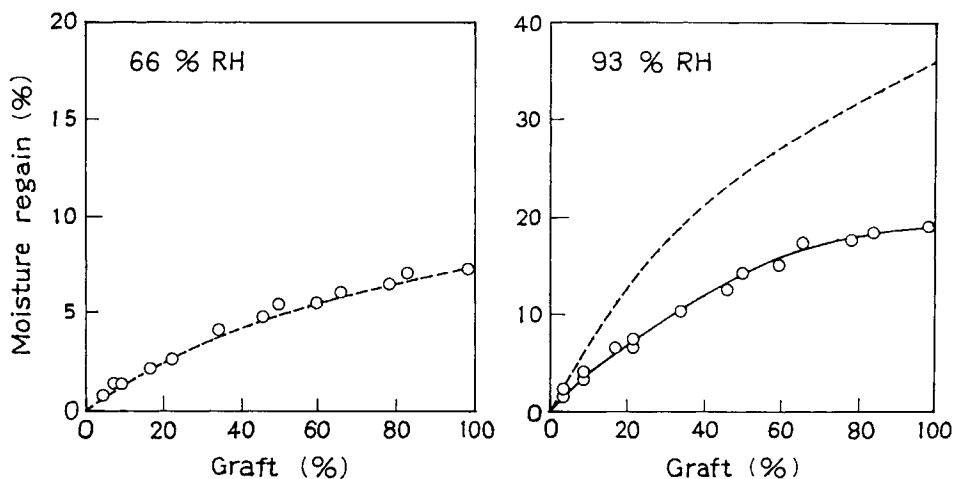


Fig. 5. Moisture regain of acrylic acid grafted foam; Broken line shows values calculated from the moisture regain of polyethylene and that of poly(acrylic acid).

The moisture regain of the grafted substance is determined by the amount of carboxylic group in the substance which is linearly related to the amount of grafted PAA chains, and is independent of the form of the substance whether it be a film, fiber, or other substance. But the data obtained for foam show that the moisture regain is a little higher than that obtained for fiber⁴ probably due to a capillary condensation effect.

The moisture regain of grafted foam in which the carboxylic groups were converted to sodium salt is also plotted as a function of graft percent by filled circles in Figure 6. It is noted from the figure that the moisture regain of grafted foam converted to sodium salt is about several times higher than that of free acid of the same graft percent.

Antistatic Properties

Improved antistatic properties of the foam are expected to result from grafting since improved hygroscopicity induced by grafting results in increased electric conductivity by the ionic conduction mechanism.

The half life of decay was measured by a static honest meter (Shishido Electric Measuring Instruments Co.). High electric field (10 kV) was applied across the foam to charge the surface up to constant potential, and the potential was then removed to measure the decay of the potential of the surface. The time required for the decay to the half value of the initial voltage was used to evaluate antistatic property.

The results are shown in Figure 7 where the half-life time is plotted as a function of graft percent at 60% relative humidity. The 50% grafting decreased the half-life of 8000 s of the original foam to only 1 s, which was short enough for the grafted foam to be used as antistatic foam. The half-life of the grafted foam converted to sodium salt was even shorter than 1 s which was below the range of the measurement.

The other method to evaluate antistatic properties by surface resistivity was carried out using a Fluke 8060A digital multimeter. The results are shown in Table I. The surface resistivity of 10^{16} ohm of the original foam decreased

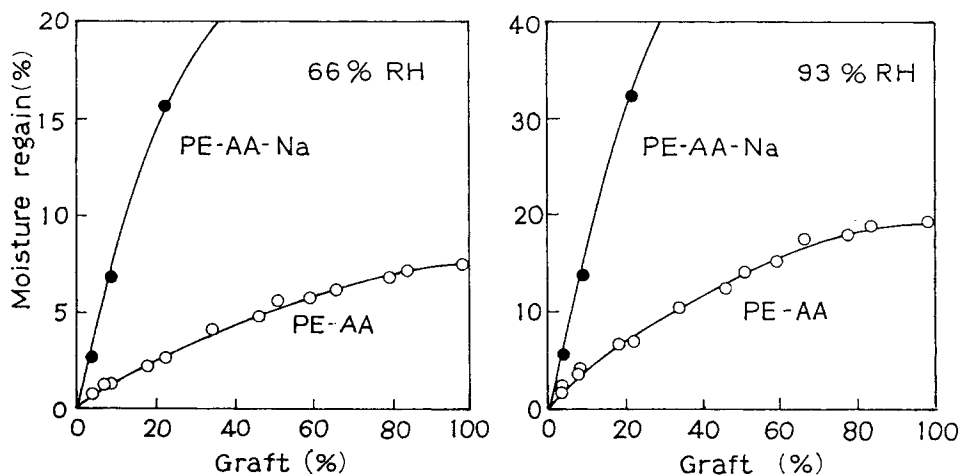


Fig. 6. Moisture regain of grafted foam as a function of graft percent: (○) Acid, (●) Na-salt.

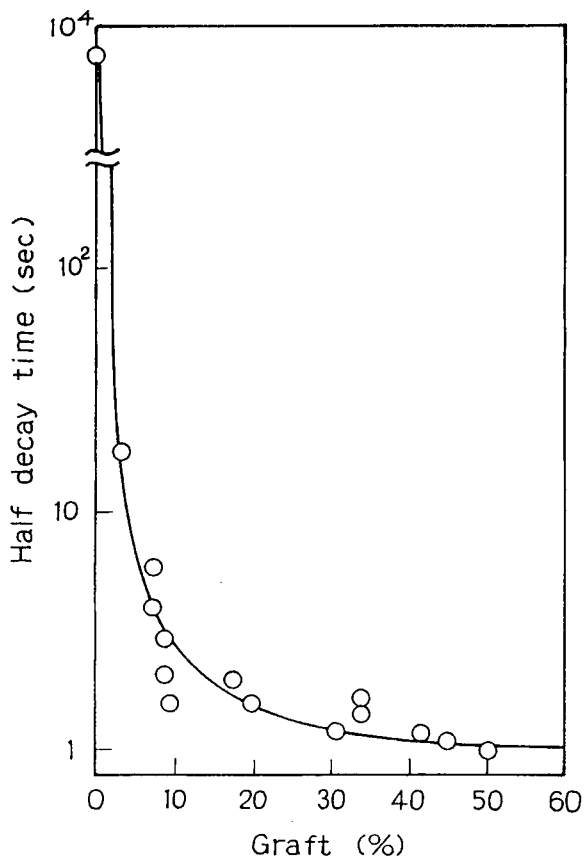


Fig. 7. Half-life of surface potential of grafted foam as a function of graft percent; Relative humidity: 60%.

TABLE I
Wicking Time^a of the Grafted Foam

Graft (%)	Wicking time ^b (s)
0.0	180 <
3.9	1 >
8.8	1 >
16.0	1 >
26.0	1 >
33.1	1 >
48.3	1 >
64.6	1 >
80.4	1 >
100.5	1 >
PVA foam	1 >

^aTime required for a droplet of water to be absorbed to foam when it is placed on a surface of the foam.

^bAverage value of six measurements for both surfaces, three on each surface.

TABLE II
Surface Electric Resistivity of Grafted Foam

	Graft (%)	Resistivity (ohm)
Starting foam	0.0	10^{16}
Acid	54.8	10^{11}
	91.9	10^{11}
Na-salt	50.4	10^6
	105.3	10^5

to 10^{11} ohm by the grafting of $\sim 50\%$ graft, which is sufficient to protect the surface from charge build-up. Resistivity was further decreased by converting the grafted foam to sodium salt: resistivities of 10^6 ohm and 10^5 ohm were obtained for grafted foam of 50% and 100% graft, respectively.

As mentioned earlier, the antistatic properties endowed by grafting result from the ionic conduction in the presence of water, and therefore, these properties may differ from those mentioned above, being somewhat poorer in the dried atmosphere.

Wicking Behavior

Wicking tests were carried out to determine the initial rate of water absorption by following three methods. The same tests were carried out for commercially available PVA foam for reference purposes. Specimens used in the tests were immersed in water and then the water was squeezed out before use.

The first test measured the time required for water droplets to be absorbed in the foam after a 0.03 mL water droplet was deposited on the foam surface from a Pasteur pipette kept 2 cm above the surface. Three measurements were taken on each side of the specimen and the average of six measurements on both sides are shown in Table II, where it is clear that the droplet on the original foam kept its shape even after 3 min, but a droplet on the 4% grafted surface disappeared quickly within 1 s. This indicates that at the grafting of graft percent as small as 4%, the initial rate of water absorption is as great as that observed for PVA foam, which is marked as water-absorbing foam.

The second test of wicking measured the time required for 1 cm vertical migration of water front after the piece of foam came in contact vertically with water surface. The results are shown in Figure 8, where 1 cm migration time is plotted as a function of graft percent. No migration of water front was observed for the original foam, but the time required for 1 cm migration was only 2–3 s for 4% grafted foam, 1.5 s for 10% grafted foam, and 1 s for 40% grafted foam which is equal to that obtained for PVA foam.

The third test measured the migration distance of water front during the first 5 s and 10 s after the foam came in contact with the water surface. The results are shown in Figure 9. Again, the original foam showed no water front migration, but 2.5 cm migration after 5 s and 3 cm after 10 s were observed for 10% grafted foam, and these values did not change when the graft percent was increased further. These values are the same as those observed for PVA foam.

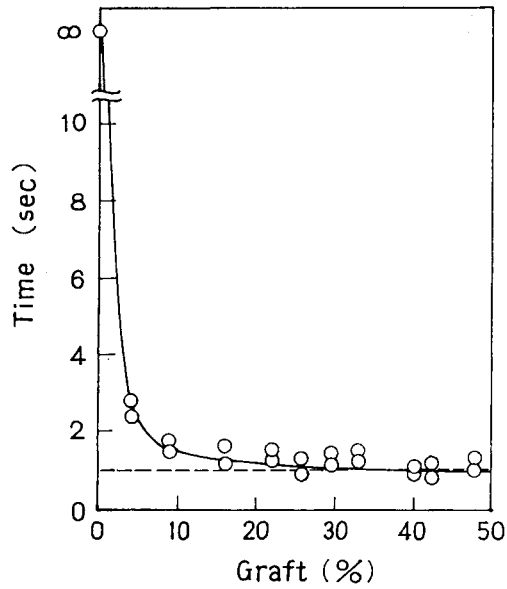


Fig. 8. Time required for first 1 cm vertical migration of water front in grafted foam; broken line indicates the data obtained for PVA foam.

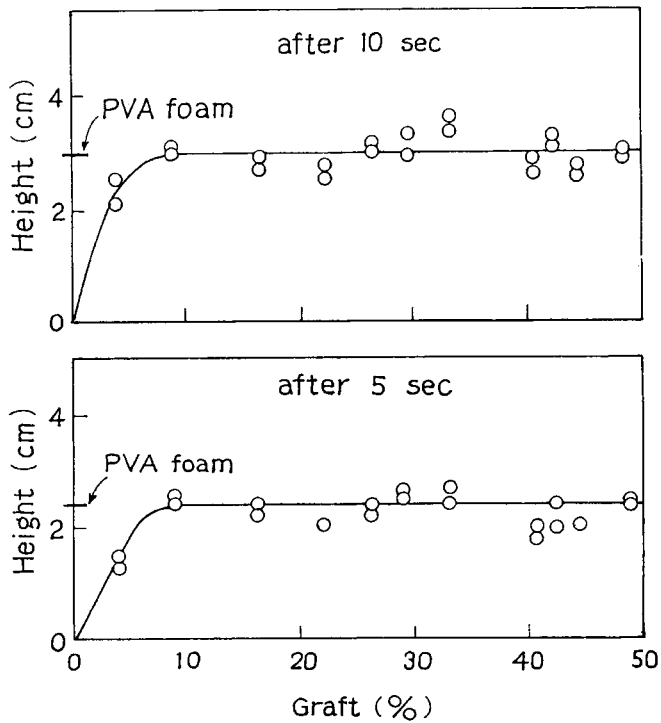


Fig. 9. Vertical migration of water front in grafted foam; dash on the ordinate indicates the data obtained for PVA foam.

All three wicking test methods agree in that significant improvement in hydrophilic properties was obtained by small graft percent, and further increase of graft percent was not necessary. This indicates that the properties of the surface are mainly determined by the functional groups on the surface, and thus sufficient improvement is attained by small graft percent if the surface concentration of the functional group is high.

Tensile Properties

We have examined whether radiation-grafting causes deterioration of the tensile properties. Tensile length and elongation were measured by an Auto-

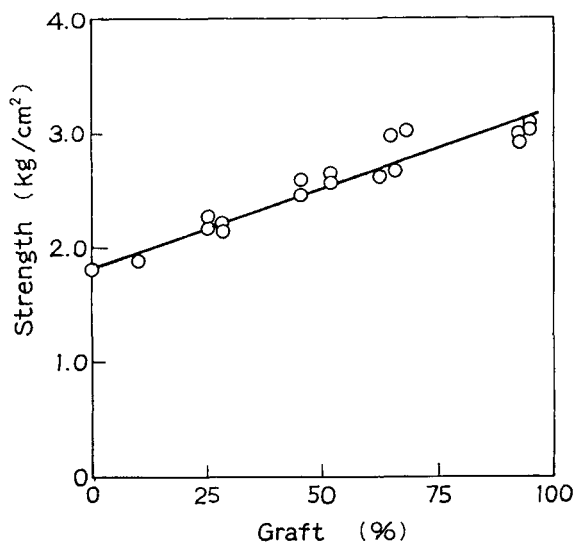


Fig. 10. Strength of grafted foam as a function of graft percent.

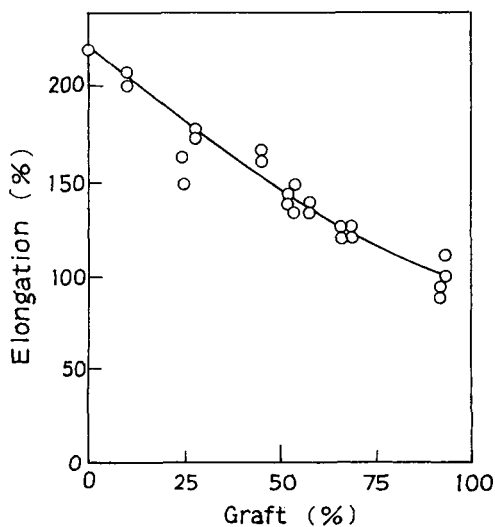


Fig. 11. Elongation of grafted foam as a function of graft percent.

graph DES-500 (Shimadzu Works Co., Ltd) at 20°C and 60% relative humidity. Sample length and crosshead speed were 40 mm and 500 mm/min, respectively. In Figures 10 and 11, tensile strength and elongation of the foam are plotted as a function of graft percent, respectively. The tensile strength seems to increase with increasing graft percent. Elongation decreased with increasing graft percent (Fig. 9) probably due to formation of hydrogen-bonding network between carboxylic groups of PAA chains.

CONCLUSIONS

By careful removal of air from the cells of polyethylene foam, grafting of acrylic acid onto polyethylene foam of open cell type was successfully performed by preirradiation technique using monomer solution containing Mohr's salt as inhibitor. Using monomer solution containing only 5% acrylic acid, grafting reaction proceeded rapidly within 15 min to reach almost level-off value of 30 graft percent, which is enough to give hydrophilic properties to the polyethylene foam.

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