

Direct Preparation of Porous Polyethylene Filters by Radiation Polymerization of Ethylene

MINORU OKADA, MASAOKI TAKEHISA, SUEO
MACHI and AKIBUMI DANNŌ, *Takasaki Radiation
Chemistry Research Establishment, Japan Atomic Energy
Research Institute, Takasaki 370-12, Japan*

Synopsis

In order to prepare porous, macroscopically homogeneous filters without a separate packing process, ethylene was polymerized by radiation in glass tubes. The bulk density of the polyethylene is approximately proportional to $\bar{\rho}_M(\bar{f}_M)^2 I^0.9 t^2$, where $\bar{\rho}_M$ is average ethylene density, \bar{f}_M is average ethylene fugacity, I is radiation dose rate, and t is reaction time. The effect of the bulk density on "treatment capacity" was investigated by experiments where air samples containing 0.1 wt-% iodine vapor were filtered. Treatment capacity is defined as that amount of air per gram of polyethylene which passes through a filter until the polyethylene reaches the break point. The treatment capacity is approximately constant at 9×10^2 cm³/g over the bulk density range from 0.03 to 0.07 g/cm³, and it is lower at the outside of this range. The pressure drop due to the polyethylene filters varies with the 2.7th power of the bulk density when the bulk density is more than 0.03 g/cm³; below 0.03 g/cm³ this exponent increases with decreasing bulk density. Because of both the necessity of high treatment capacity and that of low pressure drop, the optimum bulk density of polyethylene in the filter is about 0.03 g/cm³.

INTRODUCTION

It is known that fine powder of polyethylene can be made from ethylene by use of ionizing radiation at a temperature below its melting point. When the radiation polymerization is carried out to a high conversion (more than 10%) in a batch system, porous polyethylene is formed. Since the specific surface area of such polyethylene is very large, it may be used as filter material. As for porous polyethylene filters, low bulk density gives rise to channelling and high bulk density brings about high pressure drop. Channelling or high pressure drop can be fatal to a filter. Therefore, before carrying out the various tests of adsorption and of filtering on polyethylene filters, trial preparation and filtering experiment are made in the present work in order to determine the optimum bulk density of directly packed, porous polyethylene as polymerized.

EXPERIMENTAL

Material

The ethylene monomer used was high-purity ethylene (99%; CO-free, H₂S-free) containing about 50 ppm C₂H₂ and about 3 ppm O₂.

Preparation

Gamma ray-induced polymerization of ethylene was carried out by the following steps, where various periods of irradiation were used to form polyethylenes of various bulk densities:

(1) Six or seven glass tubes of 0.7-cm inner diameter and 11-cm length are put together in a 316 stainless-steel autoclave. (2) The autoclave is swept out with ethylene six times and then charged with ethylene to a pressure of about 4.0×10^2 kg/cm². (3) Ethylene is irradiated with ⁶⁰Co γ -rays at about 4.7×10^4 R/hr at room temperature for a certain period between 1.5 and 5.0 hr. (4) The ethylene pressure is reduced slowly to the atmospheric pressure in such a manner that the pressure is reduced by half in at least 20 min (if the decrease in pressure is not slow enough porous polyethylene shrinks). (5) The glass tubes are taken out of the autoclave and polyethylene around the tubes and in the vicinity (about 0.5 cm) of their ends is removed. (6) The tubes, which can now be called "polyethylene filters," are weighed to calculate polyethylene bulk densities.

Measurements

To determine the optimum bulk density, a mixture of air and iodine is considered to be one of the most suitable gas samples, because iodine vapor is either easily adsorbed or easily detected. Therefore, iodine vapor was used in the experiment. The iodine content of the sample used was determined after filtering experiments by use of the weight increase of the filters. Filtering experiments were carried out in the following way using the apparatus illustrated in Figure 1:

(1) Air is passed through water and then contacted in a 1.1-liter flask with iodine crystals at atmospheric pressure and at about 21°C to form an air sample containing water vapor and iodine vapor. (2) The air sample is sucked to suction system B (Fig. 1, structure 5). After 2.2 liters of air has been sucked through, the air flow is directed to the filter to be tested. The air flow gives a reddish color to the filter. On leaving the filter, the air flow narrows and comes into contact with wet potassium iodide starch paper. The flow rate is kept approximately constant during one run, but each run has, in most cases, short interruption periods (at every 10²-cm³ passage of air) to allow for the resetting of suction system A. (3) The flow is stopped soon after the violet spot which appears on the starch paper comes to a certain depth. If the run continues for more than an hour, it is necessary to rewet the starch paper halfway.

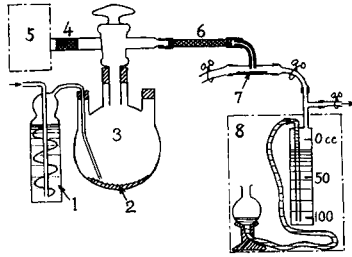


Fig. 1. Apparatus for filtering experiment: (1) water; (2) iodine; (3) 1.1-liter flask; (4) activated charcoal; (5) suction system B; (6) filter to be tested; (7) potassium iodide starch paper; (8) suction system A.

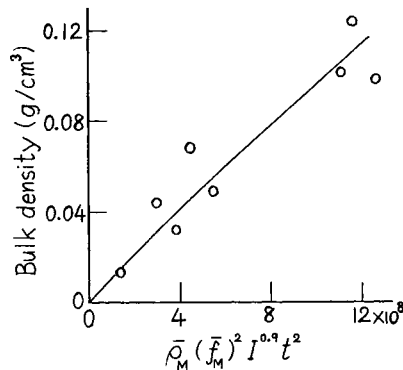


Fig. 2. Bulk density vs. $\bar{\rho}_M(\bar{f}_M)^2I^{0.9}t^2$ ($\bar{\rho}_M$ in g/cm³; \bar{f}_M in kg/cm²; I in R/hr; t in hr.)

Pressure drops due to the filters were measured by use of a usual U-tube manometer.

RESULTS AND DISCUSSION

It can be foreseen that the bulk density of polyethylene is proportional to the amount of ethylene polymerized in a constant volume reactor. An empirical expression for the amount of ethylene polymerized was reported previously,¹ as follows for the case when conversion is low:

$$M_p = k_1 \rho_M f_M I^{0.9} t^2 \tag{1}$$

where M_p is the amount of ethylene polymerized, k_1 is constant, ρ_M is ethylene density, f_M is ethylene fugacity, I is dose rate, and t is the reaction time. Though the conversion is not low in the present work, there may still be some relationship between polyethylene bulk density and $[\rho_M f_M^2 - I^{0.9} t^2]$. Therefore, the bulk densities were plotted against $[\bar{\rho}_M (\bar{f}_M)^2 I^{0.9} t^2]$ in Figure 2, where

$$\bar{\rho}_M = (\rho_{M_i} + \rho_{M_f})/2 \tag{2}$$

$$\bar{f}_M = (f_{M_i} + f_{M_f})/2. \tag{3}$$

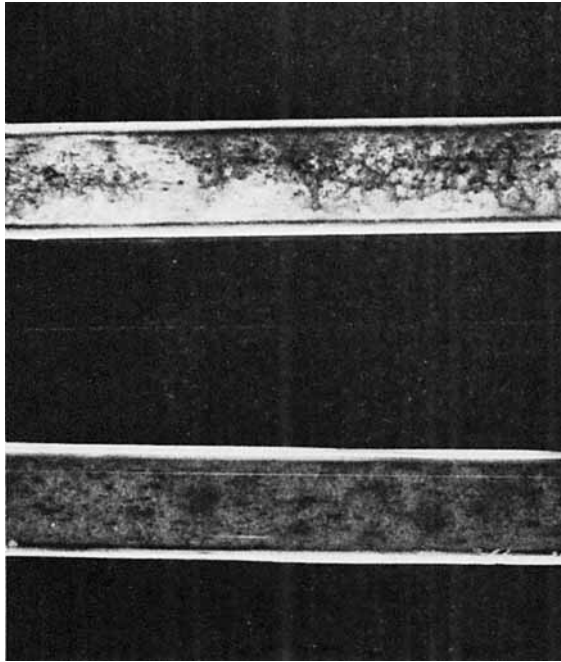


Fig. 3. Polyethylene filters held to light: upper, 0.014 g/cm³ polyethylene; lower, 0.030 g/cm³ polyethylene.

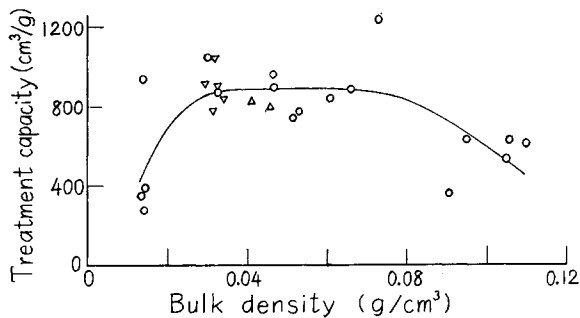


Fig. 4. Treatment capacity vs. bulk density: (∇) $0.004 < u_{\rho_b} < 0.01$; (O) $0.01 \leq u_{\rho_b} \leq 0.03$; (Δ) $0.03 < u_{\rho_b} < 0.05$.

In eqs. (2) and (3) the suffixes *i* and *f* mean initial and final, respectively. As can be seen in Figure 2, polyethylene bulk density is approximately proportional to $\bar{\rho}_M(f_M)^2 I^{0.9} t^2$.

One can see with the naked eye that polyethylene is not homogeneous when its bulk density is less than 0.03 g/cm³. Figure 3 shows polyethylene filters which are held to the light.

Bulk density variation due to dose rate distribution in the autoclave was observed when the center of the autoclave, 3.4-cm inner diameter and 6.5-cm outer diameter, was placed at 20 cm from the center of the hollow-

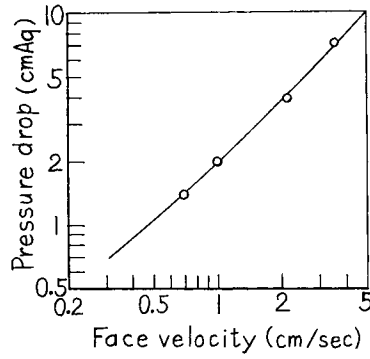


Fig. 5. Pressure drop vs. face velocity: bulk density, 0.014 g/cm³; polyethylene length, 10.5 cm; polyethylene diameter, 0.7 cm.

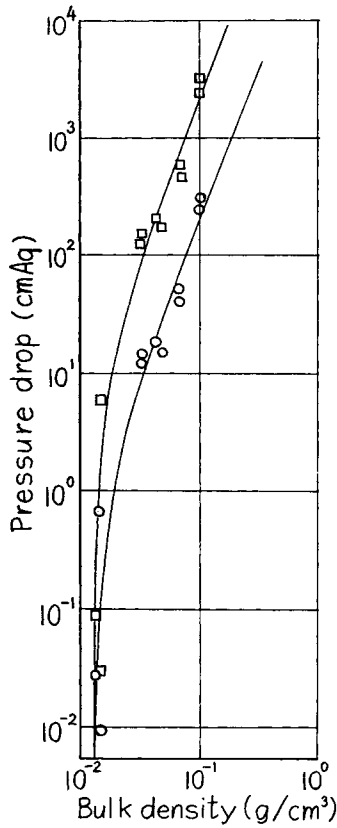


Fig. 6. Pressure drop vs. bulk density: polyethylene length, 10 ± 1 cm; polyethylene diameter, 0.7 cm; (□) u , 3 cm/sec; (O) u , 0.3 cm/sec.

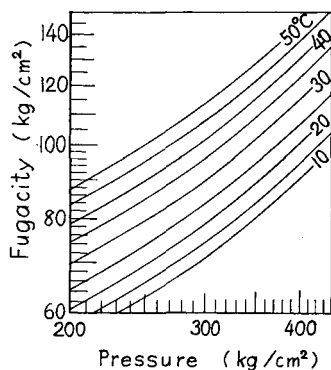


Fig. 7. Data of ethylene fugacity used in Figure 2.

cylinder cobalt-60 source. The diameter of the hollow cylinder was 14 cm. The bulk density of polyethylene varied $\pm 8\%$.

A term "treatment capacity of polyethylene" was defined, for convenience, as follows: that amount of air per gram of polyethylene which passes through a polyethylene filter of 10-cm length until the filter reaches the break point. Treatment capacity was found to be nearly constant within the bulk density region between 0.03 and 0.07 g/cm³ and lower at the outside regions, as is shown in Figure 4. The low treatment capacity at small bulk density in Figure 4 is due to channelling, and the low treatment capacity at large bulk density can be supposed to be due to the decrease of effective surface area.

Since the air flow rates were largely different from run to run, a modified flow rate was defined, for normalization, as the product of face velocity u , in cm/sec, and the bulk density of polyethylene, ρ_b , in g/cm³. In order to compare with each other the treatment capacities of polyethylenes which vary widely in their bulk densities, the use of this product will be in closer touch with reality than the use of face velocity alone. Figure 4 shows that the treatment capacity is little affected by air flow rate within the flow rate range that was used in the experiment.

The iodine content of the air sample used was determined to be about 0.10 wt-%. Accordingly, the amount of iodine adsorbed by the polyethylene which corresponds to the highest level (9×10^2 cm³/g) of the curve in Figure 4 is about 1.2×10^{-3} g/g polyethylene.

The pressure drops of each filter were measured and plotted against face velocity using logarithmic scales on both coordinates. An example of the curves obtained is shown in Figure 5. On such curves the pressure drops corresponding to certain face velocities were read out and plotted against bulk density (Fig. 6). It is seen in Figure 6 that pressure drop due to polyethylene filters increases with increasing bulk density, and that the pressure drop varies with the 2.7th power of the bulk density when the bulk density is more than 0.03 g/cm³; below 0.03 g/cm³ this exponent increases with decreasing bulk density.

It is desirable that polyethylene in filters has high treatment capacities and that pressure drops due to the filters are small. As can be seen in Figure 4, treatment capacity is high when bulk density lies between 0.03 and 0.07 g/cm³. Figure 6 shows that pressure drop decreases with decreasing bulk density. Therefore, the optimum bulk density for filter material polyethylene can be deduced to be about 0.03 g/cm³.

The data of ethylene fugacity used in Figure 2 are shown in Figure 7. The main part of Figure 7 is the plot of data obtained by Machi and Hagiwara²; the rest was obtained by inter- and extrapolation.

References

1. S. Machi, M. Hagiwara, M. Gotoda, and T. Kagiya, *Bull. Chem. Soc. Japan*, **39**, 675 (1966).
2. S. Machi and M. Hagiwara, private communication.

Received August 14, 1969