# Chlorinated Organics Removal from Water by Plasma-Graft Filling Polymerized Membranes

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In pervaporation, a membrane is placed between the liquid and the vapor, and the difference in the chemical potential between the two phases drives permeation. This process can separate azeotropic mixtures and mixtures close to boiling point. Recently, some pervaporation systems were applied for separation of small amounts of organic solvents from contaminated water (Brun et al., 1985; Lee et al., 1989a,b; Blume et al., 1990; Boddekker et al., 1990; Hoshi et al., 1991). The main purpose of this system is to solve an environmental pollution problem and to recover a valuable product. Although pervaporation systems are competitive with other conventional methods (Blume et al., 1990), the treatment cost by pervaporation depends seriously on the membrane separation properties.

A concept of filling polymerized membranes was proposed to prevent membrane swelling in organic/organic separations (Yamaguchi et al., 1991). The filling polymerized membrane proposed is composed of two materials: the porous substrate and the filling polymer which fills the pores of the substrate. The porous substrate is inert to organic liquids, and the filling polymer is soluble with one component in the feed. The filling polymer exhibits permselectivity due to the solubility difference, and the porous substrate matrix restrains the swelling of the filling polymer due to its mechanical strength. The filling polymerized membrane could be prepared by the plasma-graft polymerization technique. Plasma treatment can form polymer radicals in the porous substrate, and then successive graft polymerization can form grafted polymers in pores of porous substrate (Yamaguchi et al., 1995). Thus, the membrane solubility and swelling properties can be controlled by choosing the grafted polymer and the substrate, respectively. The membranes have showed high permselectivity for organic/organic liquid's separation (Yamaguchi et al., 1991, 1992, 1993).

It was reported that this type of membrane showed high separation properties for removal of dissolved organics from water (Yamaguchi et al., 1994). Methylacrylate, ethylacrylate and *n*-butylacrylate (BA) were employed as the grafting monomers, and the filling type membranes were prepared by plasma-graft polymerization technique. Ethylacrylate grafted membranes and BA grafted membranes showed high selectivity for chlorinated organics from water. The BA grafted membrane showed higher selectivity and permeability than a cross-linked BA membrane in literature (Hoshi et al., 1991). The grafted chains which filled in pores were linear, and the free volume of the grafted polymer might be larger than cross-linked polymer whose chain mobility was reduced by cross-linking. Moreover, swelling of the filling polymer was effectively suppressed by the porous substrate matrix. So, the filling type membrane showed both high selectivity and permeability. The order of selectivity for chlorinated organics was methylacrylate < ethylacrylate < BA grafted membranes. The order is in good agreement with the grafted polymer hydrophobicity (Yamaguchi et al., 1994). In this study, more hydrophobic polymers were used as the grafted polymer, such as poly(ethylhexylacrylate) (EHA), poly(laurylacrylate) (LA) and poly(stearylacrylate) (SA). 1,1,2-trichloroethane (TCE) was used as a model organic of halogenated hydrocarbon contaminants.

## Experimental Studies

### *Materials*

Porous high density polyethylene (HDPE) film was used as a porous substrate. The HDPE substrate of 6 $\mu$m in thickness and 0.02 $\mu$m in pore size based on a cutoff experiment was supplied by Tonen Chemical Co. Ltd.

Ethylhexylacrylate (EHA), laurylacrylate (LA) and stearylacrylate (SA) were used as the grafted monomer. EHA was purified by distillation under vacuum, and the other two monomers were used without purification. The monomers were emulsified in water with sodium dodecylbenzenesulfonate (SDS). The monomer solutions were degassed by repeated freezing and thawing.

### *Plasma treatment and graft polymerization*

The grafting process has been described in detail elsewhere (Yamaguchi et al., 1994). The conditions of plasma treatment and graft polymerization are summarized in Tables 1 and 2, respectively. The grafted membranes were rinsed overnight in toluene to remove the homopolymers and the

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**Table 1. Condition of Plasma Treatment**

| Power<br>W | Time<br>s | Pres.<br>mbar | Atm. |
|---|---|---|---|
| 10 | 60 | 0.1 | Ar |

nonreacted monomers, and oven dried at 40–50°C. The amount of grafting was estimated as the weight of grafted polymer per 1 cm$^2$ porous substrate (mg/cm$^2$). The graft polymerization expands the substrate matrix and thickness (Yamaguchi et al., 1991), and the grafted membranes, with more than 1.5 mg/cm$^2$ grafting, had 20–30 $\mu$m thicknesses.

### *Separation by pervaporation*

Pervaporations of 1,1,2-trichloroethane (TCE) dilute aqueous solutions through the membranes were carried out. The effective membrane area was 19.6 cm$^2$, and the total volume of the feed liquid was about 6,000 mL. The permeate was collected in vacuum trap condensers cooled by liquid nitrogen, and then dissolved by heating. The permeate side pressures were around 0.2 torr. The total pervaporation flux was determined by the permeate weight. The organic solute in the permeate or feed liquid was extracted in *n*-hexane, and the concentrations were determined by gas chromatography using a FID detector. The pervaporation data for the initial 2h was discarded because the permeation stream was not necessarily at steady state.

## Results and Discussion

### *Membrane preparation*

Water plays an important role for the graft polymerization by plasma (Yamaguchi et al., 1991), and thus when a hydrophobic monomer is used, a high polymerization rate is obtained with the aid of an emulsion system. In a previous article, we employed ethylacrylate and BA monomer, and high polymerizations were obtained using the emulsion polymerization technique (Yamaguchi et al., 1994).

Time dependence of graft polymerization is shown in Figure 1 with the previous results of BA monomer (Yamaguchi et al., 1994). The monomer concentration was 10 wt. %, SDS concentration was 10 wt. % and the grafting temperature was fixed at 30°C. For EHA, the polymerization rate was faster than the BA results, and the weight of EHA grafted after 30 min was eight times higher than the substrate. For LA or SA, the polymerization rate was much slower than the BA results. The order of polymerization rate was methylacrylate > ethylacrylate, EHA > BA > LA > SA. A monomer which has a longer hydrocarbon chain showed a slower reaction rate.

The grafting rate increased with increasing SDS concentration between 0 and 100 g/L (Yamaguchi et al., 1994). Time dependence of graft polymerization using higher SDS concentration is shown in Figure 2. In the range between 10 wt. % and 20 wt. % of SDS concentration, the concentration did not affect the polymerization rate.

**Table 2. Conditions of Graft Polymerization**

| Monomer | Grafting Temp.<br>°C | Grafting Time<br>h | SDS Conc.<br>Wt. % | Monomer Conc.<br>Wt. % |
|---|---|---|---|---|
| EHA | 30 | 0.5–2.5 | 10 | 10 |
| LA | 30 | 1.5–40 | 10–20 | 10 |
| SA | 30 | 2–23 | 10–20 | 10 |

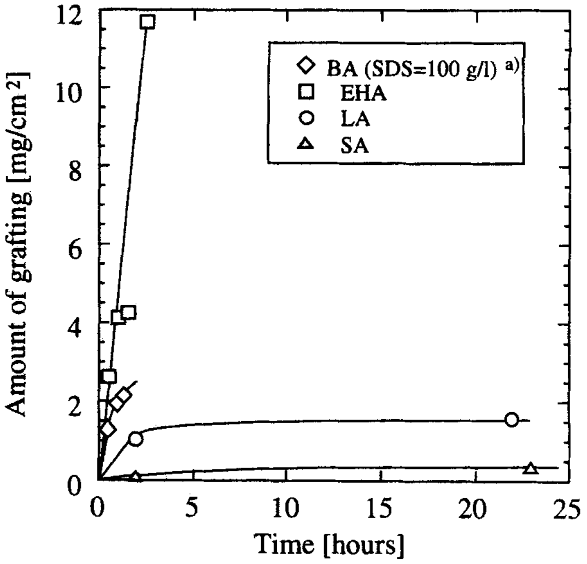

**Figure 1. Relationship between grafting time and amount of grafting.**

Monomer conc. is 10 wt.%; temperature is 30°C; SDS conc. is 10 wt. % (EHA, LA, SA), 100 g/L (BA)[4].

Although 1.5 mg/cm$^2$ grafting is needed to obtain high selectivity by pervaporation for this substrate (Yamaguchi et al., 1994), the amount of SA grafting could not reach 0.5 mg/cm$^2$ within the experimental period. Thus, data of SA grafted membrane will not be reported herein.

The grafted membranes prepared were transparent, even though the original porous substrate film was not. The refrac-

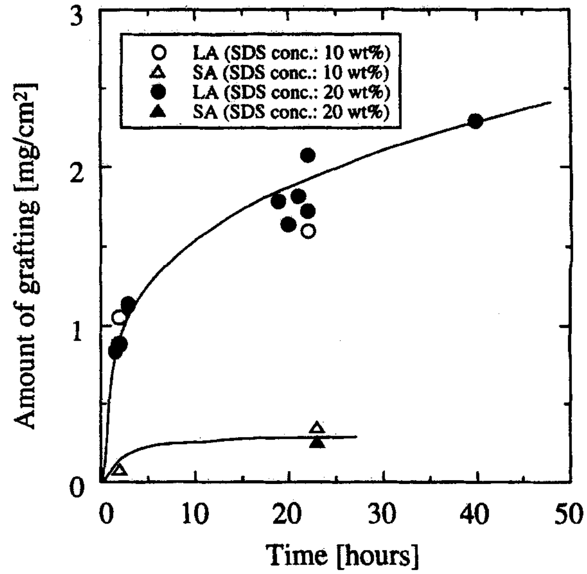

**Figure 2. Relationship between grafting time and amount of grafting.**

Monomer conc. is 10 wt.%; grafting temp is 30°C.

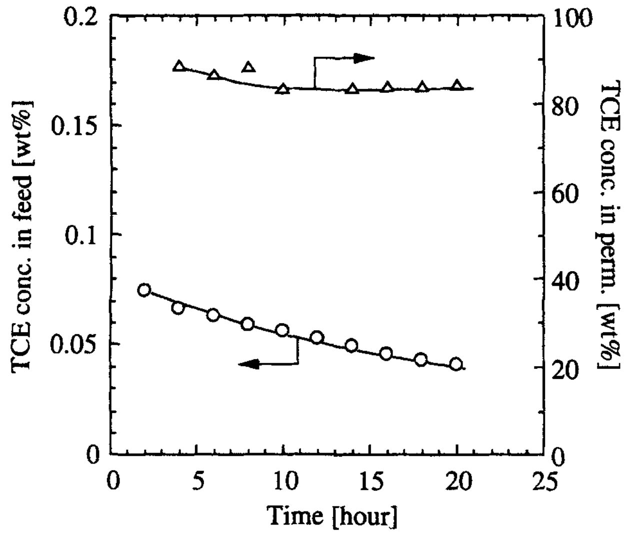

**Figure 3. Time dependence of TCE concentration in feed or permeate during pervaporation.**

Feed temp. is 25°C.

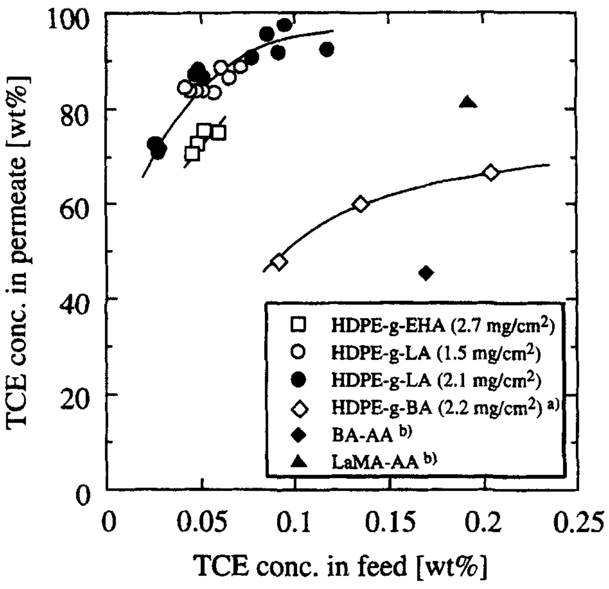

**Figure 4. Relationship between TCE concentration in feed and permeate by pervaporation.**

Feed temp. is 25°C. (a) Yamaguchi et al. (1994); (b) Hoshi et al. (1991). BA, n-butylacrylate; AA, acrylic acid; LaMA, laurylmethacrylate.

tive indexes of polymers are similar. These facts suggest that the grafted polymer filled the pores of the porous substrate resulting in a transparent membrane. Methylacrylate, ethylacrylate or BA grafted membranes are also transparent, and the grafted polymers formed in the substrate pores were verified using TEM and ATR/FT-IR analysis (Yamaguchi et al., 1991, 1994). The membranes were the filling polymerized membrane as originally proposed.

### *Pervaporation separation*

The time dependence of TCE concentration in the feed liquid and the permeate vapor is shown in Figure 3. Compositions of TCE/water feed liquid and TCE/water permeate vapor are plotted. LA grafted membrane, which had 1.5 mg/cm$^2$, was used. The membranes efficiently removed TCE from feed water, and the membrane performance was stable during the experimental period. This filling type membrane was originally prepared for organic/organic separation, and the porous substrate can suppress the membrane swelling. So, the membrane had durability against organic liquids even though the membrane was kept in pure organic liquids (Yamaguchi et al., 1992).

Dependence of TCE concentration in the feed on TCE concentration in the permeate is shown in Figure 4 accompanied with the previous results through BA grafted membrane (Yamaguchi et al., 1994), cross-linked poly(butylacrylate) or poly(laurylmethacrylate) membranes (Hoshi et al., 1991). The order of selectivity is LA grafted membrane > EHA grafted membrane > BA grafted membrane. The selectivity increased with an increase in the carbon numbers of ester groups in the grafting monomer unit. The results can be explained by an order of membrane hydrophobicity as expected. Comparing with 1.5 and 2 mg/cm$^2$ LA grafting membranes, almost the same selectivity was obtained. These results suggested that the grafted polymer completely filled the substrate pores above 1.5 mg/cm$^2$ grafting, and thus the grafting polymer density which affects the pervaporation selectivity (Yamaguchi et al., 1991, 1994) is almost the same. These LA grafted membranes showed much higher selectivity than the cross-linked membranes (Hoshi et al., 1991). The linear graft chains have large free volume compared with the cross-linked chains, and the substrate matrix could effectively suppress swelling of the grafted polymers. Thus, the filling type membranes showed both higher permeability and selectivity than the cross-linked membranes. The LA grafted membrane concentrated a 0.1 wt. % TCE aqueous solution to more than 90 wt. % TCE vapor, and the separation factor was around 10,000. The separation factor $\alpha$ was defined as follows

$$\alpha = \frac{Y/(100-Y)}{X/(100-X)} \tag{1}$$

where $X$ and $Y$ are TCE concentration (wt. %) in feed liquid and permeate vapor, respectively. The condensed permeate vapor was separated into TCE rich and water rich phases.

The dependence of TCE concentration in the feed on the TCE partial flux is shown in Figure 5. The partial flux of $i$ component $J_i$ was defined as follows

$$J_i = J_{\text{total}} \, C_{i\,\text{in perm}} \tag{2}$$

where $J_{\text{total}}$ is total pervaporation flux through a membrane, and $C_{i\,\text{in perm}}$ is concentration of $i$ component in permeate vapor. Although LA or EHA grafted membranes showed higher selectivity than the BA grafted membrane, all of membranes showed almost the same fluxes within the experimental range. These filling type membrane showed much higher flux and permeability than the cross-linked membranes (Hoshi et al., 1991). Compared with thin poly(dimethylsiloxane) or polyolefin composite membranes (Blume et al., 1990), the LA

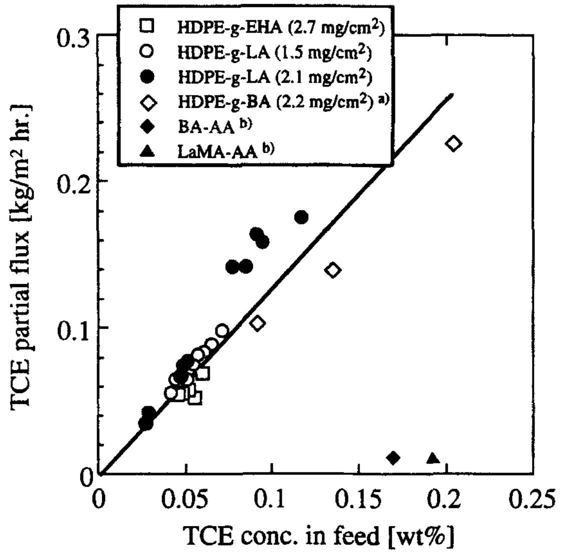

**Figure 5. Relationship between TCE concentration in feed and TCE partial flux.**

Feed temp. is 25°C. (a) Yamaguchi et al. (1994); (b) Hoshi et al. (1991). BA, n-butylacrylate; AA, acrylic acid; LaMA, laurylmethacrylate.

grafted membranes showed much higher selectivity and somewhat higher TCE partial flux.

## Conclusions

Pervaporation membranes were prepared for the removal of dilute organics from water by plasma-graft filling polymerization technique, and the following conclusions were obtained.

(1) EHA, LA and SA were used as grafting monomers. For EHA and LA, both monomers could graft efficiently with the aid of an emulsion system by the plasma-graft polymerization technique. The grafting rate of SA, however, was extremely slow, and SA grafted membrane with high grafting amount could not be obtained.

(2) Pervaporation separation of dilute aqueous solutions of TCE through EHA or LA grafted membranes were carried out. The membranes showed very high TCE selectivity and flux. The order of TCE selectivity was BA grafted membrane < EHA grafted membrane < LA grafted membrane. Both the TCE selectivity and flux through the LA grafted membrane was higher than the reference data.

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