

Adsorption and Desorption Properties of Grafted Polyethylene Films with Iminodiacetate Groups to Metal Ions and Their Regeneration

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Iminodiacetate (IDA) groups as a chelate-forming group were introduced to glycidyl methacrylate-grafted polyethylene (PE-g-PGMA) films with disodium iminodiacetate in an aqueous solution of 55 % DMSO at 80 °C, and adsorption and desorption properties of IDA-(PE-g-PGMA) films to Cu²⁺ ions were investigated as a function of the grafted amount, pH level, and temperature. The amount of absorbed Cu²⁺ ions increased with an increase in the pH value in the range of 1.0 to 5.0 and the time required for adsorption equilibrium decreased with an increase in the temperature. The desorbed amount increased and the time required for desorption equilibrium decreased with an increase in the HCl concentration. The quantities of Cu²⁺ ions of about 100% were desorbed above the HCl concentration of 0.5 M. The adsorbed and desorbed amounts were the almost same in each cyclic process of adsorption in an aqueous CuCl₂ solution at pH 5.0 and desorption in an 1.0 M HCl solution. It was made clear that the IDA-(PE-g-PGMA) films were used as a repeatedly generative chelating membrane for adsorption and desorption of Cu²⁺ ions.

Key words: polyethylene, photografting, glycidyl methacrylate, chelating adsorption, iminodiacetate group

1. INTRODUCTION

Membrane technology is now targeting the development of novel membranes with high functionality. The introduction of an ion-exchange group and affinity ligand into the membranes enables us to remove undesirable ions from wastewater [1]. We have prepared functional membranes with practical mechanical strength by the photografting technique of ionic, functional, or reactive monomers into polyethylene (PE) or expanded and porous poly(tetrafluoroethylene) (ePTFE and pPTFE) films [2-7]. The grafting techniques with UV rays are mainly applied to modify the polyolefins, because they have certain advantages in that the techniques make it easy to control the site of the grafted polymer chains and the density of the functional groups [2, 4-7]. Since one end of a grafted polymer chain is covalently bonded to a site on the polymer substrate and the other end is usually not put under restraint, grafted polymer chains have the high mobility in a good solvent and positively or negatively chargeable groups affixed to the grafted polymer chains will function as a fixed carrier to transport solutes across the membranes in the medium [4, 5].

Our work has been geared toward studying the application of grafted PE, pPTFE, and ePTFE films to functional membranes for the separation, concentration, and recovery of various ionic and neutral compounds in response to the temperature [2], pH level [4, 7], and electrical field [5, 6]. Recently, the necessity for heavy metal ion recovery processes in industrial and environmental applications and the subsequent reuse of these metal ions have led to an increasing interest in selective ion exchange [8, 9]. A novel objective of our study is to introduce a chelate-forming group to the grafted PE films by the subsequent functionalization and examine adsorption and desorption properties of the chelating membranes and their reusabilities. In addition, a membrane system is a practical alternative to the bead

system conventionally used for adsorption and separation in facile handling.

In this study, a monomer with an epoxy group, glycidyl methacrylate (GMA) was photografted with the PE films because of the facile introduction of chelate-forming groups through the ring-opening reaction of epoxy groups. Here, the chelating membranes containing iminodiacetate (IDA) groups were prepared through a simple one-step reaction with disodium iminodiacetate (IDA2Na). Adsorption and desorption properties of the resultant chelating membranes were investigated as a function of the grafted amount, pH level, and temperature.

2. EXPERIMENTAL

2.1 Photografting and chelating functionalization

A PE film (thickness, 30 μm; density, 0.924 g/cm³) supplied from Tamapoly Co. Ltd., (Japan) was used as a polymeric substrate. GMA was photografted into the PE film in an aqueous 80 vol% ethanol solution of GMA (1.0 M) according to the procedure described in our previous papers [10, 11].

The GMA-grafted PE (GMA-g-PE) films were immersed in the aqueous DMSO solutions containing IDA2Na (0.425M), and then the reaction solutions were heated at 80 °C with a moderate stirring to convert an epoxy group to a chelate-forming IDA group. The conversion from epoxy to IDA groups was calculated from the weight increase before and after the reaction.

2.2 Adsorption and desorption

The weighed IDA group-appended PE-g-PGMA (IDA-(PE-g-PGMA) films (10 × 10 mm) were placed in 100 cm³ of CuCl₂ buffer solutions (10 mM) of different pH levels at 30 °C. Amount of adsorbed Cu²⁺ ions was calculated from the Cu²⁺ ion concentration of the surrounding solution spectrophotometrically determined. Desorption properties were examined in the

HCl solutions of different pH levels in the same way as described above.

3. RESULTS and DISCUSSION

3.1 Membrane properties of IDA-(PE-g-PGMA) films

GMA-grafted PE (PE-g-PGMA) films of different grafted amounts were prepared by varying the UV-irradiation time in an aqueous 80 vol% ethanol solution of GMA monomer of 1.0 M at 60 °C. The PE-g-PGMA films of 14.1 mmol/g-PE film were immersed in the solutions of 0.425 M IDA2Na in the aqueous DMSO solutions of the DMSO volume fraction ranging from 40 to 55 vol%. The reaction was carried out at 80 °C for 24 hrs with a moderate stirring to convert epoxy groups into IDA groups. Figure 1 shows the change in the conversion with the DMSO volume fraction in the solvent. The conversion into IDA groups increased with an increase in the volume fraction of DMSO because the presence of DMSO enhanced the reaction of epoxy groups with IDA2Na through the mechanism of SN2 [1]. However, when the DMSO volume fraction went up to over 60 %, IDA2Na did not completely dissolve in the solvents.

The PE films were expanded by the photografting of GMA and the subsequent conversion of epoxy groups into IDA groups and the introduction of IDA groups yielded the water-adsorptivity to the PE-g-PGMA films. The changes in the area ratio and the amount of absorbed water with the grafted amount are shown in Figure 2 (a) and (b), respectively. The photografting of GMA led to the expansion of the PE film. It is suggested from these results that the internal grafting, which occurs simultaneously with the surface grafting, cause the expansion of the PE film [10]. The subsequent conversion of epoxy groups into IDA groups (conversion: ca 90 %) offered the water-absorptivity to the PE-g-PGMA films and their further expansion as shown in Figure 2 (b). Since the conversion into IDA groups was limited to 60 to 65 % in the study performed by Yamaguchi et. al [12], the remaining epoxy groups were converted into diol groups with sulfuric acid to enhance the hydrophilicity. On the other hand, in this study, the conversion into IDA groups went up to 90 % both by increasing the molar fraction of DMSO in the solvent and by prolonging the reaction time. Therefore,

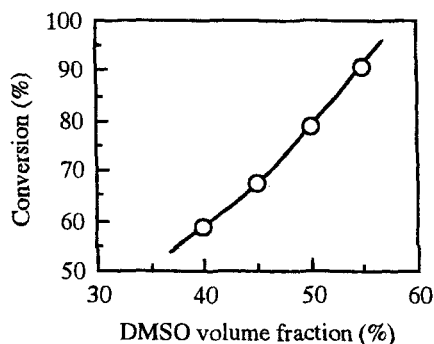


Figure 1 Change in the conversion of epoxy into IDA groups with the DMSO volume fraction in the solvent : Grafted amount = 14.1 mmol/g-PE, Concentration of IDA2Na = 0.425 M, Temperature = 80 °C, Reaction time = 24 hrs.

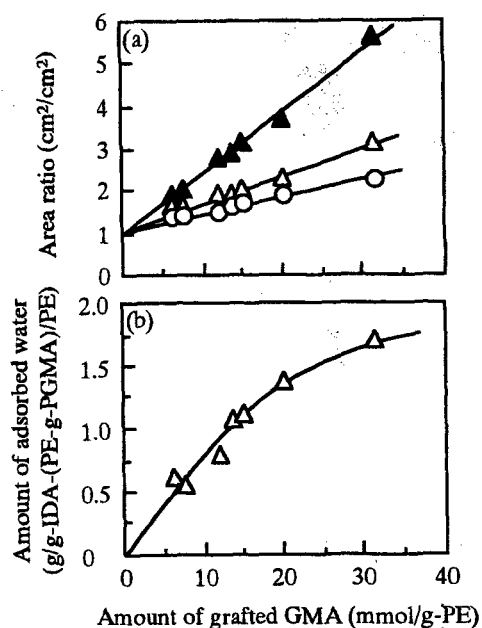


Figure 2 Changes in (a) the area ratio and (b) the amount of adsorbed water for IDA-(PE-g-PGMA) films with the grafted amount; area ratio- \circ : PE-g-PGMA/PE, Δ : IDA-(PE-g-PGMA)/PE, \blacktriangle : water-swollen IDA-(PE-g-PGMA)/PE.

the IDA-appended PE-g-PGMA (IDA-(PE-g-PGMA) films prepared here possessed high water-absorptivity as shown in Figure 2 (b) and the remaining epoxy groups were not converted into epoxy groups.

3.2 Dependence of Cu^{2+} ion adsorption on the grafted amount

The Cu^{2+} ion adsorption measurements were carried out as a function of the immersion time at pH 5 using IDA-(PE-g-PGMA) films with the grafted amounts from 10 to 50 mmol/g-PE film (conversion: 90.7 %). The amount of adsorbed Cu^{2+} ions increased with increasing the immersion time, and then leveled off. The degree of adsorption for each IDA-(PE-g-PGMA) film was calculated from the amount of adsorbed Cu^{2+} ions at equilibrium and the degree of conversion into IDA groups. In addition, the kinetic constants of adsorption were calculated from the slope of the linear relationship between the immersion time and $\ln(1-Q_t/Q_{eq})$ value [7]. Figure 3 shows the changes in the degree of adsorption and the kinetic constant of adsorption, k , with the grafted amount. The amount of adsorbed Cu^{2+} ions increased with the grafted amount over the grafted amount and the degree of adsorption and the value of the kinetic constant of adsorption became constant above the grafted amount of 15 mmol/g-PE film. The limitation of Cu^{2+} ion adsorption to 75 % is probably due to the restriction of diffusion of Cu^{2+} ions into the inside the grafted layers.

3.3 Dependence of Cu^{2+} ion adsorption on the pH level

The IDA-(PE-g-PGMA) films with the grafted amount of 14.1 mmol/g-PE film were immersed in the buffer solutions of CuCl_2 of 1.0 mM at the pH levels of 1.0 to 5.0 at 30 °C. Figure 4 shows the change in the

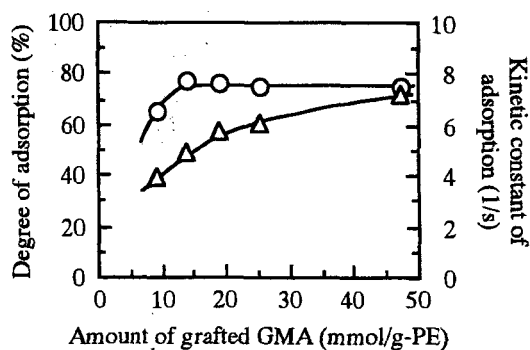


Figure 3 Changes in the degree of adsorption (○) and the kinetic constant of adsorption (△) with the grafted amount at pH 5 and 30 °C : Conversion = 90.7 %, Concentration of CuCl₂ = 1.0 mM.

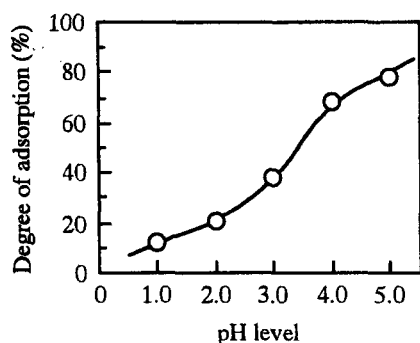


Figure 4 Change in the degree of adsorption with the pH level of an aqueous CuCl₂ solution at 30 °C : Grafted amount = 14.1 mmol/g-PE, Conversion = 90.7 %, Concentration of CuCl₂ = 1.0 mM.

degree of adsorption with the pH level. The degree of adsorption increased with the pH level and went up to 77 % at pH 5.0. The increase in the pH level promotes the dissociation of carboxylic groups in the IDA groups from $-N(\text{COOH})_2$ to $-N(\text{COO}^-)_2$, which is responsible for the chelating adsorption of Cu²⁺ ions. The values of the kinetic constant of adsorption were kept constant irrespective of the pH level.

3.4 Dependence of Cu²⁺ ion adsorption on the CuCl₂ concentration

The CuCl₂ concentration dependence of the Cu²⁺ ion adsorption was investigated in the CuCl₂ concentration of 0.05 to 2.0 mM at 30 °C. Figure 5 shows the change in the degree of adsorption determined from the amount of IDA groups in the IDA-(PE-g-PGMA) film and the amount of adsorbed Cu²⁺ ions with the initial CuCl₂ concentration. The degree of adsorption increased with an increase in the initial CuCl₂ concentration, particularly sharply below 0.5 mM. The equilibrium CuCl₂ concentration and the amount of adsorbed Cu²⁺ ions bore a linear relationship in Langmuir adsorption isotherm equation. This result means that Cu²⁺ ions are bonded to IDA groups in the 1:1 stoichiometry through the mechanism of chelating. The value of the kinetic constant of adsorption increased from $4 \sim 5 \times 10^5$ (s) in the range of the CuCl₂ concentration of 0.05 to 2.0 mM.

3.5 Dependence of Cu²⁺ ion adsorption on the

temperature

The temperature dependence of the Cu²⁺ ion adsorption was investigated in the 1.0 mM CuCl₂ buffer solutions of pH 5.0 in the range of the temperature from 20 to 50 °C. Figure 6 shows the changes in the degree of adsorption and the time required to reach the adsorption equilibrium with the temperature. The time required to reach the equilibrium adsorption was shortened with the temperature, although the degree of adsorption was independent of the temperature. Therefore, the value of the kinetic constant of adsorption increased with the temperature.

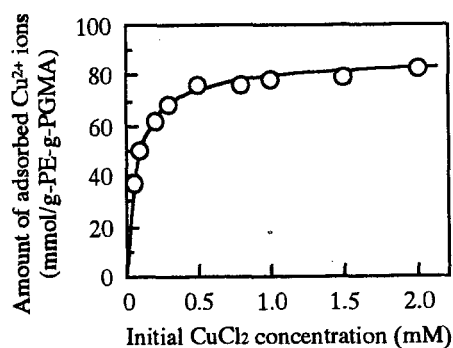


Figure 5 Change in the amount of adsorbed Cu²⁺ ions with the initial CuCl₂ concentration at pH 5.0 and 30 °C : Grafted amount = 14.1 mmol/g-PE, Conversion = 90.7 %.

3.6 Dependence of Cu²⁺ ion desorption on the HCl concentration

The effect of HCl concentration on the desorption of Cu²⁺ ions by immersing the IDA-(PE-g-PGMA) films (Grafted amount = 15.3 mmol/g, conversion = 81.6 %) which had reached the adsorption equilibrium at pH 5.0 in the aqueous HCl solutions of 0.05 ~ 1.0 M at 30 °C. The desorbed amount increased with the immersion time, and then leveled off irrespective of the HCl concentration. Figure 7 shows the changes in the degree of desorption calculated using the amounts of adsorbed and desorbed Cu²⁺ ions and the time required to reach the desorption equilibrium with the HCl concentration. The degree of desorption increased and the time required

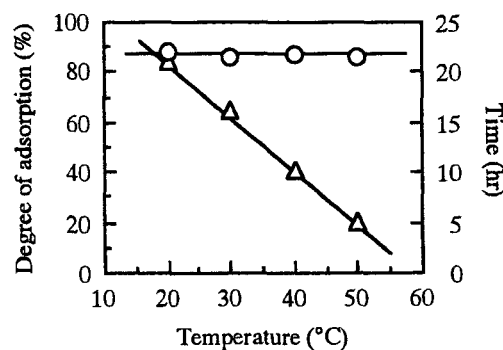


Figure 6 Changes in the degree of adsorption (○) and the time required to reach the equilibrium adsorption (△) with the temperature : Grafted amount = 15.3 mmol/g-PE, Conversion = 81.6 %, Concentration of CuCl₂ = 1.0 mM.

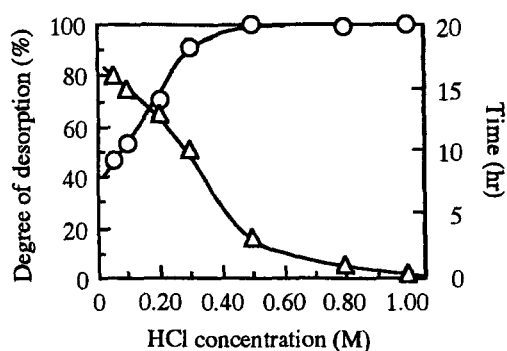


Figure 7 Changes in the degree of Cu^{2+} ion desorption (\bigcirc) and the time required to reach the desorption equilibrium (\triangle) with the HCl concentration: Grafted amount = 15.3 mmol/g-PE, Conversion = 81.6 %, temperature = 30 °C.

for the desorption equilibrium was shortened with an increase in the HCl concentration. The quantities of Cu^{2+} ions of about 100 % were desorbed above the HCl concentration of 0.5 M. Since the chelation occurs between dissociated IDA ($-\text{N}(\text{COO}^-)_2$) groups and Cu^{2+} ions, the decrease in the pH level, which results in the depression of the dissociation of IDA groups level, lead to the increase in the desorption of Cu^{2+} ions.

3.7 Repetitive cycles of adsorption and desorption

On the basis of the results on the pH dependence of both adsorption of Cu^{2+} ions as shown in Figure 3 and desorption as shown in Figure 5, the cyclic process of adsorption at pH 5 and desorption in 1.0 M HCl solution was alternately repeated an IDA-(PE-g-PGMA) film. Figure 8 shows the three successive Cu^{2+} ion adsorption-desorption cycles. The adsorbed and desorbed amounts were almost equivalent in each cyclic process of adsorption and desorption. These results indicate that the IDA-(PE-g-PGMA) film is practically acid-proof and can endure several cycles of adsorption and desorption experiments without considerable fatigue.

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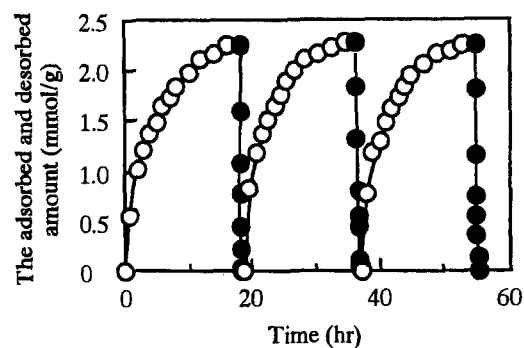


Figure 8 Alternately repeated cyclic process of adsorption at pH 5.0 (\bigcirc) and desorption in 1.0 M HCl (\bullet): Grafted amount = 14.1 mmol/g-PE, Conversion = 81.6 %, Concentration of CuCl_2 = 1.0 mM, Temperature = 30 °C.

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