Evaluation of PE/PP-GMA fabric for the Adsorption of Lead and Lithium Ions: A Study on Selectivity and Performance

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Abstract: The radiation-induced graft polymerization method is discussed. In this study, a PE/PP fabric was irradiated with a 10 kGy electron beam, followed by the grafting of glycidyl methacrylate (GMA) using a graft polymerization method to produce PE/PP-g-GMA fabric. The epoxy groups of the GMA grafted side chains were subsequently converted to sulfonate groups, forming PE/PP-g-GMA-Na_2SO_3. The physical and morphological properties of the adsorbent were analyzed using Fourier transform infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM). The PE/PP-g-GMA-Na_2SO_3 fabric demonstrated effective adsorption of lead (Pb^{2+},) and lithium (Li^+) from solutions with concentrations of 100 ppb and 1 ppm in pure and mixed systems at different pH levels (3, 5, 7). The concentration of metal ions in the solutions was determined using Inductively Coupled plasma optical emission spectroscopy (ICP-OES) and Inductively coupled plasma mass spectrometry (ICP-MS), confirming the fabric's adsorption efficiency. The experiment was crucial for enhancing fellows' understanding of the practical and theoretical aspects of radiation-induced graft polymerization. This research was conducted at the Takasaki Institute for Advanced Quantum Science, QST in Takasaki , Japan.

Keywords: PE-polyethelene; PP-polypropylene,; wt%-weight percent; emulsion graft polymerization, dissolved oxygen; metal adsorbent; glycidyl methacrylate

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I. INTRODUCTION

Graft polymerization method is a unique modification technique that combines a polymer material (trunk polymer) with another polymer chain (graft chain) by using active species (ionic or radical sites) generated on the polymer material. Generically, radiation-induced grafting consists two basic processes, namely an irradiation process and a grafting reaction process.

The degree of grafting depends on many factors, such as the type of polymer and monomer, monomer concentration, type of radiation, temperature, reaction atmosphere, concentration of homo polymerization suppressor and type of solvent [1].

I have explored using PE/PP fabrics as metal adsorbents through radiation-induced graft polymerization techniques, including electron beams and γ-rays. This paper discusses a comprehensive laboratory experiment that encompasses graft polymerization, conversion reactions, and the adsorption of lithium (Li^+) and lead (Pb^{2+}) ions using PE/PP fabrics. Throughout my research, I utilized various sophisticated scientific instruments such as ICP-MS, SEM, and FTIR, gaining hands-on training in data collection, interpretation, and material characterization under the guidance of laboratory mentors.

Additionally, I investigated how varying experimental parameters, including absorbed dose, reaction time, and solvent composition, influenced the GMA-grafted PE/PP fabrics with diverse GMA chain densities. This program provided a valuable opportunity to engage with both basic and advanced technologies, as well as hands-on experiments at highly developed research facilities, such as the electron beam accelerator facility at TIARA [2].

II. MATERIAL AND METHODS

2.1 PE/PP-fabric preparation

A non-woven polyethylene (NWPE) fabric obtained from Kurashiki Textile Manufacturing Co.,Ltd.(Osaka, Japan) was used as a trunk polymer for graft polymerization. The average diameter of the NWPE fabric was 13 μm. Four sheets of PE/PP fabrics (size:3x5 cm; average weight:110 mg) were packed into a gas barrier bag. After the gas barrier bag was sealed under vacuum, the PE/PP fabrics were irradiated using a electron beam source at -79ºC (dry-ice). The irradiated PE/PP fabrics were then stored in a -80 ºC freezer until use.

2.2 Preparation of stock solution

In this study, a 100g solution was prepared by thoroughly mixing 5 wt% of glycidyl methacrylate (GMA) monomer, 0.5 wt% of Tween 20 (polysorbate 20, supplied by Kanto Chemical Co., Inc., Tokyo, Japan), and 94.5 wt% of distilled water. Lead nitrate and a lead standard solution for quantitative analysis (1000 ppm), as well as ultra-pure nitric acid (Ultrapure-100), were also sourced from Kanto Chemical Co., Inc.

All commercial chemicals were of reagent grade and used without further purification. Deionized water from a Milli-Q deionization system (Nihon Millipore K.K., Tokyo) was used to prepare the monomer emulsion and sample solutions.

2.3 Radiation source

Irradiations were carried out using an low energy e-beam. The electron beam irradiation facility are often used for surface treatment of polymer materials. The energy of the electron beam used for processing varies depending on the thickness of the material and the desired result.

2.4 Radiation Induced Graft polymerization

In this section, we conducted experiments on the procedure of radiation-induced graft polymerization [3] under optimal conditions. The monomer emulsion of 5wt% GMA was prepared by adding GMA to a 0.5wt% Tween 20 aqueous solution that was then stirred at room temperature for 5 min. After bubbling with nitrogen to displace dissolved oxygen in the GMA emulsion, 120mL of the de-aerated GMA emulsion was poured into a test tube contained.

The grafting reaction was carried out by keeping the sealed test tube in a 40 ºC water bath. The reaction time were varied 15 min. Residual monomers and homopolymers were removed by washing the resulting GMA-grafted PE/PP (PE/PP-g-GMA) fabrics with water and methanol.

The amount of GMA grafted into the PE/PP fabric was evaluated by the degree of grafting Dg (%) was calculated using the following equation.

$$\text{Degree of grafting: } D_g(\%) = \frac{(W_1 - W_0)}{W_0} \times 100 \qquad (1)$$

where W_1, W_0- are the dry weights of the PE/PP fabrics before and after grafting, respectively.In this study, we aimed to reach a grafting reaction rate of 150–200 %. For this purpose, after conducting several experiments, the sample was irradiated with a 10 kGy electron beam and heated at 40°C for 15 minutes, which was identified as the optimal condition for the grafting reaction experiment.

Table 1. *Degree of grafting*

	W_0	W_1	D_g[%]	Average	Standard devition	Reaction Time [min]
1	0.0862	0.2425	181.3225	195.3912	12.48778	15
2	0.0862	0.2438	182.8306			
3	0.0804	0.2481	208.5821			
4	0.0839	0.2582	207.7473			
5	0.0831	0.2517	202.8881			
6	0.0889	0.2569	188.9764			

2.5 Conversion of epoxy group to sulfonic acid group

For that experiment, the epoxy group was converted to the sulfonic acid group. The prepared solution of 600 ml with sodium sulfite Na2SO3 dissolved in isopropyl alcohol (IPA) and water had a composition of Na2SO3:(IPA):water equal to 6:10:50 wt%. The grafted PE/PP fabric with GMA was immersed in Na_2SO_3 solution at 80 ºC for a period ranging from 20 h. The fiber was taken out and repeatedly washed water and methanol.

$$Conversion(\%) = \frac{(W_2 - W_1)x142}{(W_1 - W_0)x120.6} \times 100 \qquad (2)$$

W_2- weight of the PE/PP-g-GMA- Na_2SO_3 fabric.

142,103.6- molecular mass of GMA, Na_2SO_3, respectively.

Table 2. *Conversion reaction*

	W_0	W_1	Dg [%]	Reaction time[h]	W_2	$Ymol$	$Xmol$	Conversion (%)
1	0.0670	0.1885	181.3		0.2686	0.000773	0.000856	90.36946
2	0.0670	0.1890	182.3		0.2746	0.000826	0.00086	96.13129
3	0.0652	0.2011	208.5	20	0.2988	0.000943	0.000957	98.52812
4	0.0665	0.2046	207.7		0.3017	0.000937	0.000973	96.36808
5	0.0725	0.2095	188.9		0.3061	0.000932	0.000965	96.65788

The following expression was used to calculate Y_{mol}; X_{mol}:

$$Y_{mol} = W_2 - W_1/103.6$$

$$X_{mol} = W_1 - W_0/142$$

2.6 Heavy metal Adsorption test

Polyoxyethylene sorbitan monolaurate (Tween 20), used as a surfactant in the preparation of the monomer emulsion, was provided by Kanto Chemical Co., Inc. (Tokyo, Japan). Additionally, a lead standard solution (1000 ppm) and ultrapure nitric acid (Ultrapure-100) were used. In this study, we prepared a 100 g solution by thoroughly mixing 5 wt% GMA monomer (glycidyl methacrylate), 0.5 wt% Tween 20, and 94.5 wt% distilled water.

In our metal absorbent study, we have selected lithium (Li) as a representative rare metal and lead (Pb) as a toxic heavy metal

The adsorption amount , q_e was measured using following equation:

$$q_e = (C_o - C_e)\frac{V}{m} \quad [mg/g] \qquad (3)$$

C_e- concentration of solution $[ppm,\ mg/l]$

C_o-initial concentration of solution $[ppm,\ mg/l]$

V-volume of solution $[ml]$

m- dry weight of PE/PP fabric $[mg]$In the batch test, a 1 cm diameter of PE/PP-g-GMA- Na_2SO_3 (~30mg) was prepared volume of solution (50 mL) of 100ppb, 1ppm Li, Pb, Li/Pb mix each solutions at different pH values (pH=3,5 and 7) for 1h, 24h at room temperature (25ºC)

III. RESULTS AND DISCUSSION

3.1 Infrared Spectroscopy-FTIR

In this work, the physical and morphological properties of the absorbent were studied using FTIR and SEM. Figure 1 illustrates the FT-IR spectra of the cotton fabric, the grafted cotton fabric and the modified cotton fabric with sulfoinc acid groups. Infrared spectroscopy was analyzed using a Perkin-Elmer Frontier, Yokohama, Japan in the range from 400-4000 cm^{-1}.

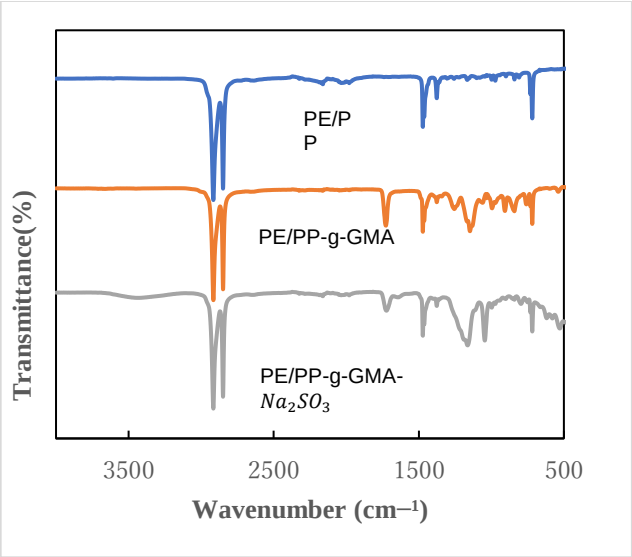

Figure 1. *FTIR of (a) cotton fabric blank, (b) grafted cotton fabric with GMA, (c) chemically modified poly-GMA with sulfonic acid group;*

Figure 1a (PE/PP) shows the FT-IR spectrum of the original cotton fabric. According to the FT-IR spectrum, the GMA-grafted fabric (1b) exhibits C=O and C-O-C stretching bands at 1264, 950-815, and 755 cm^{-1}, which are attributed to the epoxy group. Following the conversion reaction (1c), these bands disappear, and characteristic absorption bands of the sulfate group, with O-H stretching oscillations, emerge in the regions of 1249, 1034, and 655 cm^{-1}. This indicates that the PE/PP-g-GMA material has undergone a successful conversion from epoxy groups to sulfate groups after the reaction

3.2 Scanning Electron Microscope-SEM

In Figure 2, a comparison is shown between the ungrafted PE/PP sample, the PE/PP-g-GMA sample after grafting reaction, and the PE/PP-g-GMA-Na2SO3 sample after the chemical reaction with sodium sulfate, using Scanning Electron Microscopy (SEM SU3500-Hitachi) at 1000x magnification. From the micrograph of the grafted material, it can be observed that the diameter of each fiber was wider than that of the ungrafted material. For the chemically treated cotton fabric-poly-GMA with sulfonic acid (c) the fiber became thicker and covered with a smooth layer of deposits caused by the hydrophilic nature of sulfonic acid. The entire fiber also appeared to be coated with deposits as a result of the penetration and diffusion of sulfonic acid groups through the fiber.

Figure 2. *Scanning electron microscope (SEM) of (a) cotton fabric blank, (b) grafted cotton fabric with GMA,(c) chemically modified poly-GMA with sulfonic acid group*

3.3 Fabrication of Heavy Metal Adsorbent

In our metal absorbent study, we have selected lithium (Li) as a representative rare metal and lead (Pb) as a toxic heavy metal. In the batch test, a 1 cm diameter sample of PE/PP-g-GMA-Na_2SO_3 (~30 mg) was prepared. The fabric was immersed in 50 mL solutions of 100 ppb Li, 1 ppm Pb, and a Li/Pb mixture. Solutions (50mL) were sampled at 5, 15, 30, 45 ,60, 90, 120, 180, 240, and 360 min. The prepared solutions were adjusted to pH 3, 5, and 7 using a pH meter (Denver Instrument) by diluting them with standard solutions such as 50M HNO_3 and 0.025M HN_3. The concentration of Li and Pb ion in the filtered sampling solutions was measured using inductively coupled plasma optical emission spectrometry (ICP-OES; Optima 8300, Perkin-Elmer Japan, Yokohama, Japan).

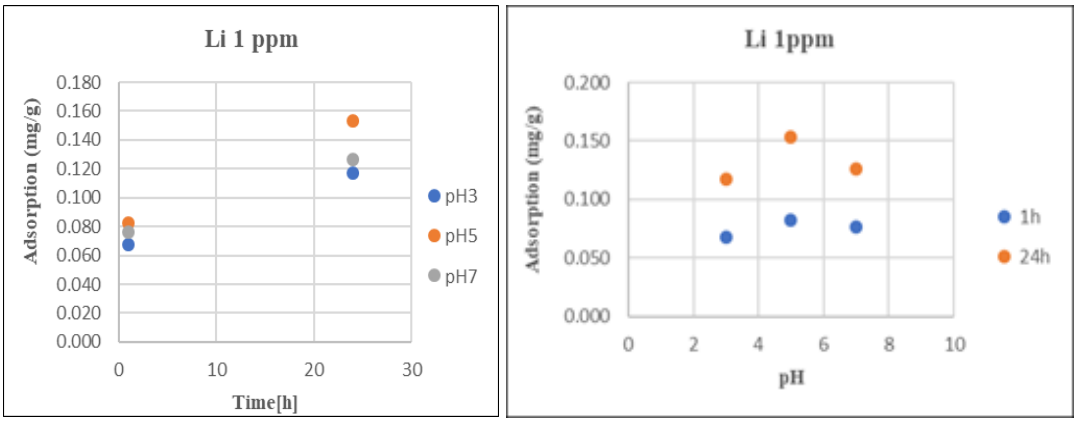

Figure 3. *Amount of Li-ion absorption depending on pH and Time*

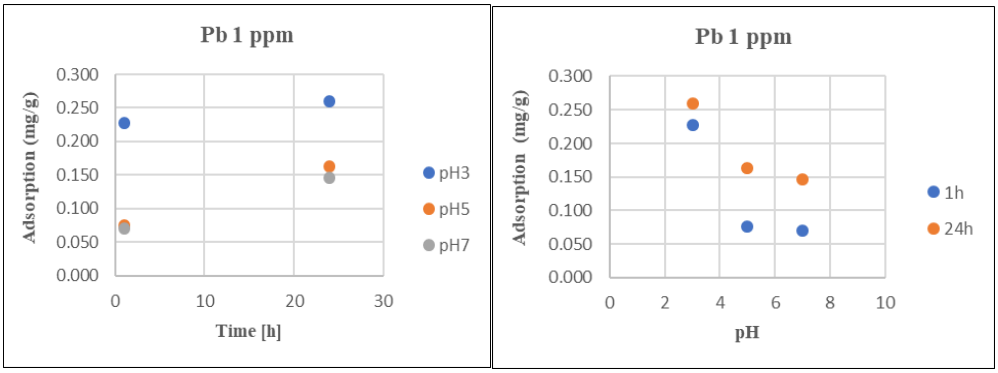

***Figure 4**. Amount of Pb-ion absorption depending on pH and Time*

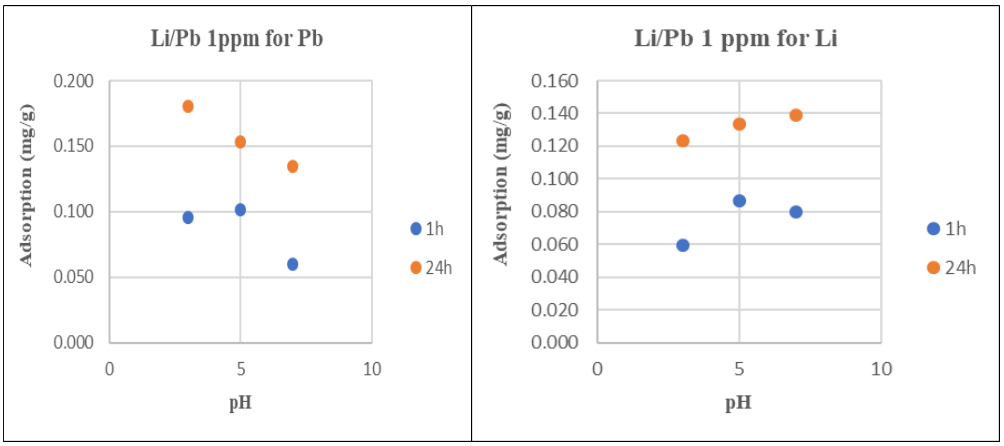

***Figure 5.** Amount of Li/Pb mixed solution of absorption depending on pH (3.5.7)*

In this study, we investigated the adsorption expirement of PE/PP-g-GMA-Na_2SO_3 fabric for Pb^{2+} and Li^{+} ions. Based on the study's findings, it is clear that the membrane has a higher selectivity for Pb2+ over Li+. Although Pb^{2+} showed a slightly higher affinity due to its larger ionic radius and lower hydration energy, this difference was not as pronounced as anticipated.

We need to conduct more experiments to investigate factors such as modifications to the membrane structure, different experimental conditions (e.g., temperature and ion concentration), and alternative metal systems. This will help us determine if these changes could result in more noticeable differences in adsorption between Pb and Li. This could yield valuable data on the selectivity of the polymer membrane for specific heavy and rare metals, thus contributing more novel insights to the field.

ACKNOWLEDGEMENT

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