

Preparation of polymer-coated separators using an electron beam irradiation

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ABSTRACT

A polymer-coated polyethylene (PE) separator was prepared by a dip-coating of PVDF-HFP/PEGDMA on both sides of a PE separator followed by an electron beam irradiation. The thermal and electrochemical properties of the polymer-coated PE separator were investigated by using FT-IR, SEM, DSC and an impedance analyzer. The results showed that the coated PVDF-HFP/PEGDMA layer was covalently bound to the PE separator and also crosslinked by an electron beam irradiation. Thermal shrinkage dramatically decreased with an increase in the absorption dose and the PEGDMA content due to the crosslinking of the coated PVDF-HFP/PEGDMA by an irradiation. The PE separator coated with the composition of PVDF-HFP/PEGDMA (9.5/0.5) and irradiated to 150 kGy showed the highest electrolyte uptake of 125% and ionic conductivity of 3.82×10^{-4} S/cm at room temperature.

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1. Introduction

Since the Almand group established a polyethylene oxide (PEO)-alkali metal salt complex as a solid polymer electrolyte (SPE) in an electrochemical device, many endeavors have been made for its practical use for lithium secondary batteries [1–3].

Liquid electrolyte (LE) as a conventional electrolyte in lithium secondary batteries has a high ionic conductivity but safety problems such as LE leakage and fire hazard. Therefore, it requires separators to prevent a direct contact between anode and cathode which causes a thermal runaway and the possibility of a LE leakage. Intrinsic SPE has excellent mechanical properties and no safety issues, such as thermal runaway and LE leakage, but a drawback of low ionic conductivity (10^{-5} S/cm) at room temperature. Many researches have been reported to overcome these problems of LE and SPE [4–10].

One of the promising approaches to overcome these problems of LE and SPE is to utilize gel polymer electrolyte. Gel polymer electrolyte (GPE) has several advantages: (1) higher ion conductivity than intrinsic SPE (10^{-3} S/cm), (2) no LE leakage, (3) adequate mechanical properties and so forth. However, commercial lithium polymer batteries still need a separator because it affords an ade-

quate ionic conductivity with adequate mechanical properties to support the winding tension of an anode/polymer polymer electrolyte/cathode in an assembly process. So far, several methods including a dip-coating, thermal treatment, UV radiation, chemical initiator, plasma treatment and high energy radiation have been utilized to fabricate polymer electrolytes for lithium secondary batteries [11–16]. Especially, a high energy radiation is an attractive technique since it technique has many advantages: (1) the polymerization proceeds mildly and thoroughly; (2) the chemistry of the reaction system is free of a contamination (no initiators are needed); (3) and the energy consumption is relatively low [17–26].

In the present study, a polymer-coated polyethylene separator was successfully prepared by a simple dip-coating of a PE separator with PVDF-HFP/PEGDMA mixture followed by an electron beam irradiation. The synthesis, chemical and electrochemical properties of the modified membranes have been described.

2. Experimental

2.1. Materials

Commercial microporous polyethylene (PE) separator (F12BMS, thickness: 12 μ m, Gurley No.: 250 s, porosity: 33%, melting tem-

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perature: 133.5 °C, crystallization temperature: 119.2 °C) made by the wet process was obtained from Tonen Chemical (Japan). Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and poly(ethylene glycol) dimethacrylate (PEGDMA, M_n : 875) were purchased from Aldrich and used as received. An electrolyte solution consisting of 1.0 M of LiClO_4 in 1:1 (v/v) ethylene carbonate (EC)/diethyl carbonate (DEC) mixture was donated from Techno-Semichem Co., Ltd. (Korea). Other chemicals were reagent grade and used as received.

2.2. Preparation of polymer-coated PE separator

PVDF-HFP and PEGDMA were dissolved in acetone at room temperature for 4 h, and the weight ratios of PVDF-HFP to PEGDMA were 10/0, 9.5/0.5, 9/1 and 8/2. Microporous PE separators were then dip-coated in the PVDF-HFP/PEGDMA solutions. The coated PE separators were sealed in PE packages and purged with dry nitrogen. The prepared separators were then irradiated by an electron beam to doses of 60, 100, 150 and 200 kGy at the dose rate of 10 kGy/pass at room temperature. After an irradiation, the irradiated separators were washed with acetone several times to completely remove the unbound PVDF-HFP and PEGDMA. Finally, the separators were dried under a vacuum at room temperature.

2.3. Liquid electrolyte uptake

The liquid electrolyte uptake was determined by an activation of the obtained separators in a liquid electrolyte solution for 24 h. To remove the excess electrolyte adhering to their surfaces, the equilibrated samples were blotted using laboratory wipes and then weighed quickly. The liquid electrolyte uptake was determined from the difference in the weights of the dried samples and their swollen counterparts. All the procedures were carried out in an Ar-filled glove box (less than 5 ppm O_2 and H_2O).

2.4. Measurements

Scanning electron microscope (SEM) investigations were carried out with Jeol SEM (model JSM-6390). The samples were dried and sputter-coated with a thin gold film prior to SEM observation. Differential scanning calorimetry (DSC) thermograms of the polymer-coated separators were obtained with DSC Q100 system of TA instrument in a temperature range of 30–200 °C at a heating rate of 5 °C/min under nitrogen atmosphere. All the samples were

sealed in aluminium pans in a glove box prior to the DSC runs. The degree of crystallinity of the polymer electrolyte (X_c) was calculated using the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_{m100}} \times 100, \quad (1)$$

where ΔH_m is the heat for melting the PE separator and ΔH_{m100} is the heat for melting the 100% crystalline PE separator, which equals 288.0 J/g. Thermal shrinkage was determined by measuring the strain changes of the samples cut in the machine direction (MD) using dynamic mechanical analyzer (DMA) as tension mode under a constant load (50 mN) in a temperature range of 30–180 °C at a heating rate of 5 °C/min under air atmosphere.

2.5. Ionic conductivity

The ionic conductivity of the separators activated with electrolyte solution at room temperature was determined by AC impedance technique over the frequency range from 0.01 to 100 kHz using a Solatron SI 1260 frequency response analyzer combined with an SI 1287 electrochemical interface. The constant potential was fixed to 10 mV. Samples with the area of A and thickness of L were sandwiched between two stainless steel blocking electrodes

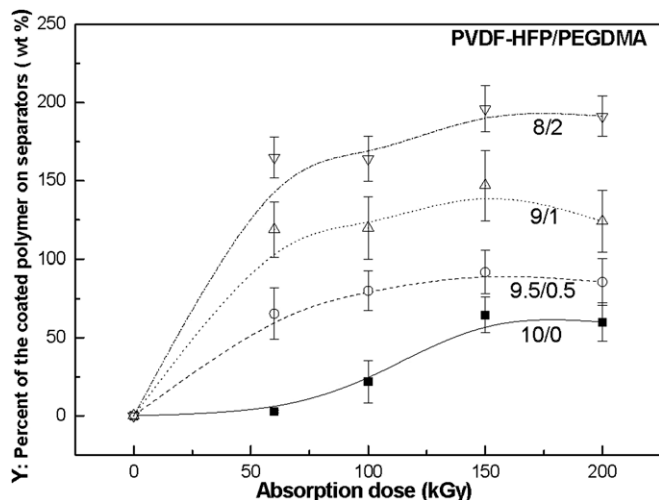


Fig. 1. The weight percent of the chemically attached polymer (PVDF-HFP/PEGDMA) on the PE separator as a function of the absorption dose.

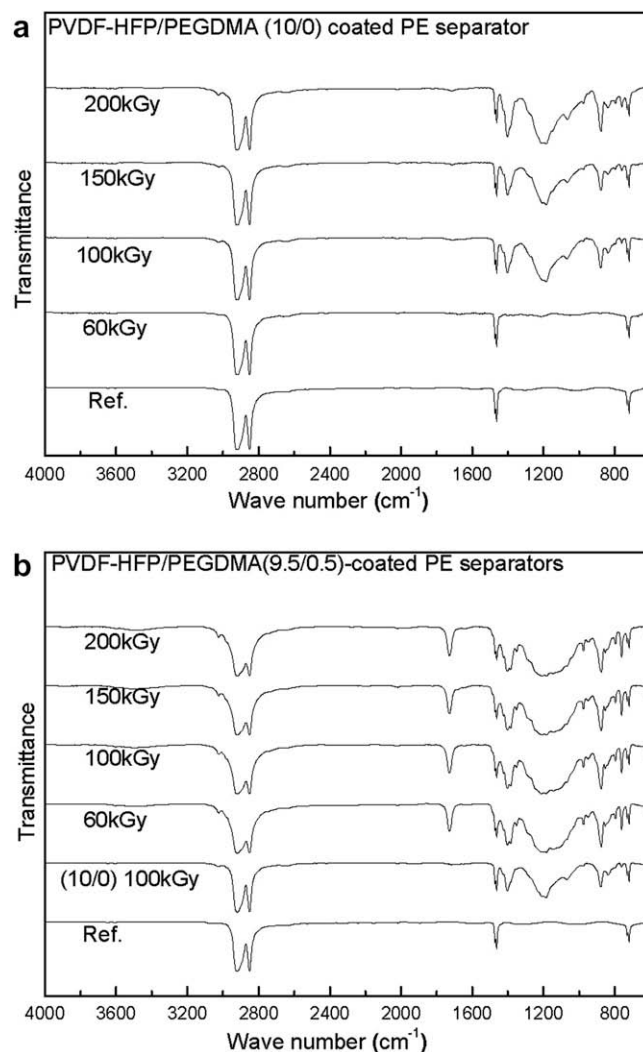


Fig. 2. Typical FT-IR spectra. (a) PVDF-HFP/PEGDMA (10/0)-coated PE separator and (b) PVDF-HFP/PEGDMA (9.5/0.5)-coated PE separator as a function of the absorption dose.

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