

## Research Article

# Effect of Addition of Soybean Oil and Gamma-Ray Cross-linking on the Nanoporous HDPE Membrane

Jong-Seok Park,<sup>1</sup> Jong-Bae Choi,<sup>1</sup> Hui-Jeong Gwon,<sup>1</sup> Youn-Mook Lim,<sup>1</sup> Myung Seob Khil,<sup>2</sup> Phil-Hyun Kang,<sup>1</sup> and Young-Chang Nho<sup>1</sup>

<sup>1</sup>Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, 1266 Sinjeong-dong, Jeongeup, Jeonbuk 580-185, Republic of Korea

<sup>2</sup>Department of Organic Materials and Fibers Engineering, Chonbuk National University, Jeongju 561-756, Republic of Korea

Correspondence should be addressed to Young-Chang Nho, jasper@hanmail.net

Received 23 February 2012; Accepted 16 April 2012

Academic Editor: Sevan P. Davtyan

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A nanoporous high-density polyethylene (HDPE) membrane was prepared by a wet process. Soybean oil and dibutyl phthalate (DBP) were premixed as codiluents, and gamma-rays were used for the cross-linking of HDPE. The pore volume of the nanoporous HDPE membranes with soybean oil was affected by the extracted amount of oil. The tensile strength of the membrane improved with an increasing absorbed dose up to 60 kGy, but decreased at 80 kGy due to severe degradation. The ionic conductivity of the nanoporous HDPE membrane did not really change with an increasing absorbed dose because the pores had already been formed before the gamma-ray radiation. Finally, the electrochemical stability of the HDPE membrane increased when the absorbed dose increased up to 60 kGy.

## 1. Introduction

A lithium secondary battery cell is generally comprised of an anode, a cathode, a nonaqueous electrolyte, and a separator, and each component in such a battery cell has been studied thoroughly to achieve the best battery performance [1, 2].

A separator is a critical component in lithium secondary batteries, and its main function is to prevent an electrical short circuit, permeate high ions, and be thermally stable and mechanically strong during an assembly operation [3, 4].

Nanoporous high-density polyethylene (HDPE) membranes are widely used as separators in Li-ion secondary batteries [5]. HDPE is one of the most important thermoplastics due to its good mechanical properties and resistance to chemicals and harsh environments [6, 7].

There are several techniques that are generally used for the fabrication of HDPE membranes, including a dry process, a nonwoven matrix, and a wet process. The dry process is relatively less expensive, and there is no solvent contamination; however, its major disadvantage is a relatively

low tear resistance to the machine direction, due to the highly oriented structure [8, 9]. Nonwoven membranes have some disadvantages, such as a large pore size and thicker nature [5]. The wet process is suitable to achieve high porosity if a stretching step is added. Also, a membrane manufactured through a wet process is nonoriented for both the pore structure and mechanical strength [10–15].

However, these polyolefin membranes have some disadvantages such as a poor compatibility with liquid electrolytes due to their hydrophobic property, and a large thermal shrinkage [3, 4]. Sufficient data have not yet been reported in the existing literature for polyolefin membranes, which have a good mechanical property and low thermal shrinkage while maintaining high porosity.

From these backgrounds, we tried to develop a membrane that has a good mechanical property and low thermal shrinkage while maintaining high porosity. The objective of this research is to report the results of a study on the role and effects of gamma-ray irradiation and soybean oil on the properties of a nanoporous HDPE membrane.

## 2. Materials and Methods

**2.1. Materials.** A commercial grade high-density polyethylene (HDPE; Hivorex 5200BH) was used throughout this study and was supplied by Honam Petrochemical Corporation (Daejeon, Korea). The alumina was supplied by Buehler Co., Ltd. (Lake Bluff, USA). The particle size and specific surface area of the alumina were 50 nm and 100.2 m<sup>2</sup>/g.

Dibutyl phthalate (DBP) and soybean oil were used as codiluents. DBP was purchased from Junsei chemical Co., Ltd. (Tokyo, Japan). Soybean oil was supplied by Sigma-Aldrich Co., Ltd. (St. Louis, USA). An electrolyte solution consisting of 1.0 M of LiClO<sub>4</sub> in a 1:1 (v/v) ethylene carbonate (EC)/diethyl carbonate (DEC) mixture was donated from Techno-Semichem Corporation (Kongju, Korea) and placed in an Ar-filled glove box. The electrodes (LiCoO<sub>2</sub> and MCMB) used in this study were purchased from the Korea Power Cell Company.

**2.2. Sample Preparation.** Soybean oil and DBP were pre-mixed as codiluents for the formation of pores. The HDPE pellets and alumina with codiluents were mixed in an extruder (Brabender D-47055) and uniaxially drawn by a roller to obtain precursor films.

The precursor films are irradiated by  $\gamma$ -ray at a dose rate of 5 kGy/hr. The irradiated films were uni-axially stretched by up to 600% in a propylene glycol bath at 120°C and then extracted by ethanol.

The mixing formulations are shown in Table 1.

**2.3. Measurements of the Samples.** The porosity and pore diameter of the samples were measured with a mercury porosimeter (AutoPore IV 9500; Micromeritics, USA). Concerning the porosity, at least three specimens were tested, and the average value was taken.

The morphological changes of the samples were observed using a scanning electron microscope (SEM; JSM6390 JEOL Company, Japan). The specimen surfaces were coated with a thin layer of gold palladium alloy by sputtering to provide a conductive surface.

The structural changes of the prepared sample were investigated by FT-IR spectroscopy (Bruker Optik GmbH, Germany).

The tensile strength was measured with an Instron443 at room temperature. The size of the specimens was 5 × 20 mm, the thickness was about 0.02 mm, and the head speed was 10 mm/min. The tensile strength of each sample was tested at least five times, and the average value was taken.

A thermal shrinkage test of the sample was conducted in an oven at 120°C for 60 min. The thermal shrinkage ( $S_h$ ) can be calculated by the following equation:

$$S_h(\%) = \frac{(A_o - A_a)}{A_o} \times 100, \quad (1)$$

where  $A_o$  is the original area of the samples before heating, and  $A_a$  is the area of the samples after heating.

To measure the ionic conductivity, the membranes were soaked in an electrolyte solution at room temperature in an

TABLE 1: Preparation conditions for the HDPE membranes.

Sample name	HDPE (wt%)	Alumina (%)	Soybean oil (wt%)	DBP (wt%)
S10	74	10	10	6
S14	70	10	14	6
S19	65	10	19	6
S25	59	10	25	6

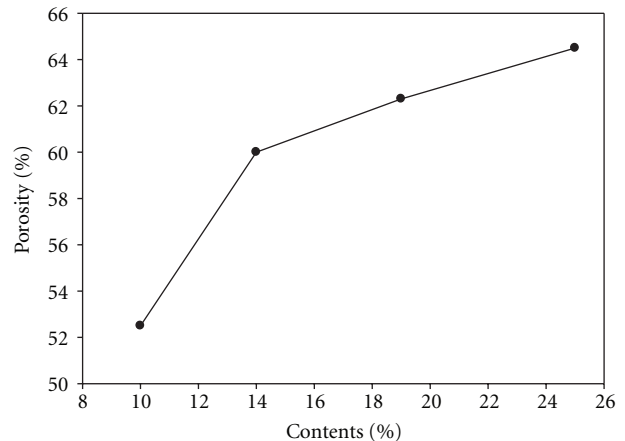


FIGURE 1: The porosity of the nanoporous HDPE membrane with soybean oil content.

Ar-filled glove box and sandwiched between two stainless steel blocking electrodes. The ionic conductivity at room temperature was determined by the AC impedance technique in a frequency range of 0.01 to 100 kHz using a Solartron SI 1260 frequency response analyzer, which was combined with an SI 1287 electrochemical interface. The constant potential was 10 mV. Samples with area ( $A$ ) and thickness ( $L$ ) were sandwiched between two stainless steel blocking electrodes to measure the electrolyte resistance ( $R_b$ ,  $\Omega$ ). The ionic conductivity ( $\sigma$ , S cm<sup>-1</sup>) was then calculated by the following equation:

$$\sigma = \frac{L}{(R_b \times A)}. \quad (2)$$

To measure the linear sweep voltammetry (LSV), the membranes soaked in a liquid electrolyte solution were sandwiched between the lithium metal and stainless steel and assembled into a tightly sealed test cell. The LSV test for the membrane was determined to be from 3.0 V to 5.5 V at 0.5 mV/sec.

## 3. Results and Discussion

As its main function, the membrane for a lithium secondary battery should be a very good electronic insulator and has the capability of conducting ions by soaking the electrolytes. Also, they should minimize adverse affects such as serious damage and thermal shrinkage [16–18].

Figure 1 shows the porosity of the nanoporous HDPE membrane with the soybean oil content. The porosity of the

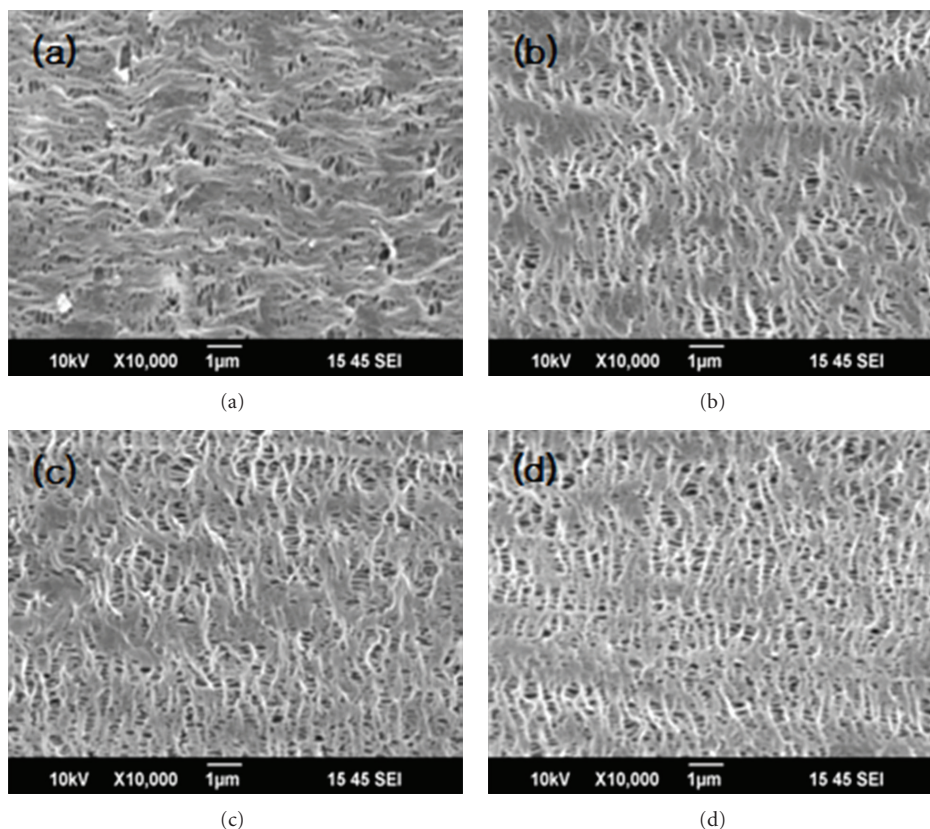


FIGURE 2: The SEM micrographs of the surface of the HDPE membrane: (a) S10, (b) S14, (c) S19, and (d) S25.

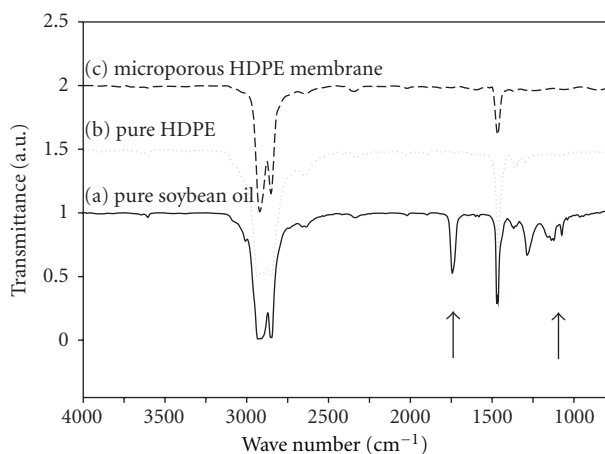


FIGURE 3: The FT-IR spectra of the HDPE membrane with soybean oil.

nanoporous HDPE membrane increased with increasing amounts of soybean oil. The porosity of the HDPE membrane containing soybean oil with 10% alumina was about 52% and that of the HDPE membrane containing soybean oil with 25 wt% was about 64%.

SEM images of the surface of the nanoporous HDPE membrane with soybean oil content are shown in Figure 2. It can be clearly seen that the nanosized pore volume on the

HDPE membranes increased with an increase in soybean oil contents. From this result, it was found that the porosity of the nanoporous HDPE membrane is directly related to the content of soybean oil. The main reason for this result is presented in Figure 3.

Figure 3 shows the FT-IR spectrums as a function of the addition of soybean oil. Figures 3(a) and 3(b) are FT-IR spectrums of pure soybean oil and pure HDPE, respectively. Figure 3(c) is the HDPE blend containing 25% soybean oil after extraction. The FT-IR spectrum of Figure 3(a) showed that a peak corresponding to the  $\text{-C=O}$  stretching vibration peak of the ester group at  $1746\text{ cm}^{-1}$ , and the  $\text{-C-O}$  stretching vibration peaks at  $1255$ ,  $1160$ , and  $1120\text{ cm}^{-1}$ , appeared. When the HDPE blend contained 25% soybean oil after extraction (Figure 3(c)), the  $\text{C=O}$  stretching vibration peak and  $\text{-C-O}$  stretching vibration peaks of the soybean oil had completely disappeared. Also, the FT-IR spectrum of Figure 3(c) is similar to that of pure HDPE (Figure 3(b)).

From these results, it was found that the pore volume of the nanoporous HDPE membranes with soybean oil was affected by the extracted extent of the soybean oil. Consequently, the pore volume of the nanoporous HDPE membranes increased with an increase in the content of the soybean oil.

Figure 4 shows the tensile strength of a nanoporous HDPE membrane with an increase in radiation dose. The tensile strength of the HDPE membrane decreased with an increase in the contents of the soybean oil due to the

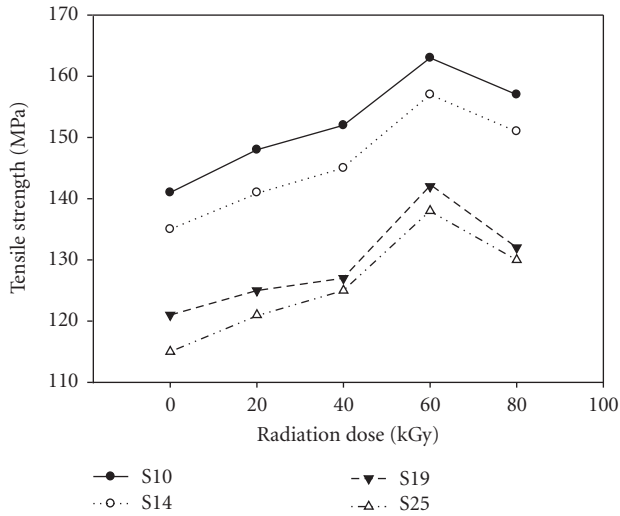


FIGURE 4: The tensile strength of the nanoporous HDPE membrane with an increasing radiation dose.

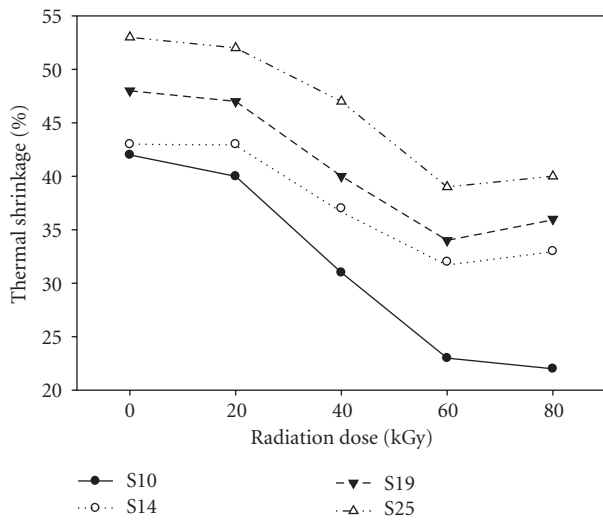


FIGURE 5: The thermal shrinkage of the nanoporous HDPE membrane with an increasing radiation dose.

increased pore volume. However, the tensile strength of the membrane increased with an increase in absorbed dose up to 60 kGy, but decreased at 80 kGy due to severe degradation. As shown in Figure 4, the high doses of irradiation induced severe degradation rather than a crosslinking of the materials.

A nanoporous film should be resistant to severe conditions such as high temperature. For example, the thermal shrinkage rate of a nanoporous film should be minimized [4]. Figure 5 shows the thermal shrinkage of the nanoporous HDPE membrane with an increase in radiation dose. As shown in Figure 5, the thermal shrinkage of the nanoporous HDPE membrane decreased with an increase in absorbed dose up to 60 kGy due to the formation of a cross-linked network in the HDPE membrane, which is caused by gamma irradiation. In addition, the thermal shrinkage of the

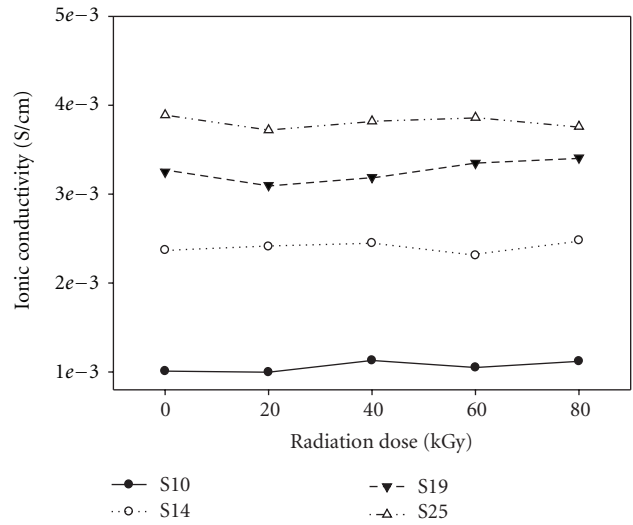


FIGURE 6: The ionic conductivity of the nanoporous HDPE membrane with an increasing radiation dose.

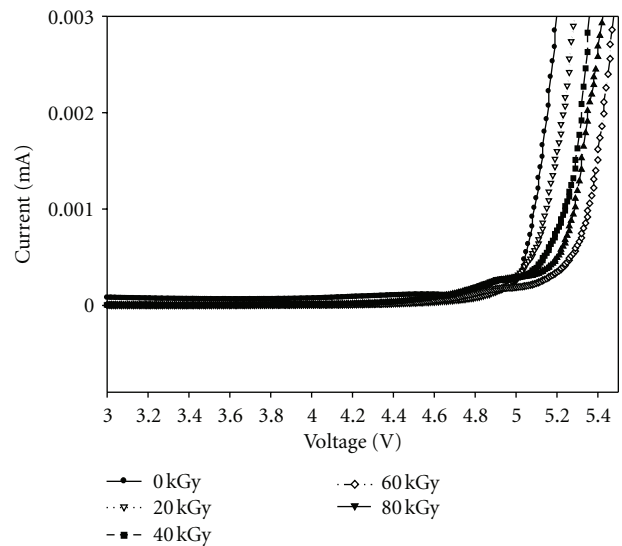


FIGURE 7: The linear sweep voltammetry (LSV) of the nanoporous HDPE membrane with an increasing radiation dose (S19).

nanoporous HDPE membrane with the same absorbed dose increased when the content of the soybean oil was increased due to the shrinkage of the increased pores in the HDPE membrane.

Figure 6 shows the ionic conductivity of the nanoporous HDPE membrane with an increase in radiation dose. The ionic conductivity of the nanoporous HDPE membrane increased with the content of the soybean oil. This result is very similar to the porosity trend of Figure 1. This can be attributed to the higher porosity and faster transportation of Li-ions through the pores in the HDPE membranes [19]. Also, the ionic conductivity of the nanoporous HDPE membrane did not really change with an increase in absorbed



dose because the pores had already been formed before  $\gamma$ -ray radiation.

The electrochemical stability of this novel membrane can be evaluated by linear sweep voltammetry (LSV). Figure 7 shows the LSV of the nanoporous HDPE membrane with an increase in radiation dose. Generally, the current-voltage study of the polymer electrolyte has been employed to determine whether the polymer electrolyte can withstand the operating voltage such as 3–4.2 V of the battery system. As shown in Figure 7, all of the irradiated HDPE membrane in a test cell shows a good electrochemical stability on the anode up to 5.2 V, while the nonirradiated HDPE membrane shows oxidation stability on the anode up to 5.0 V. The irradiated HDPE membrane, especially at 60 kGy, exhibited anodic stabilities of up to 5.4. These results clearly indicate that the irradiated HDPE membrane can withstand electrolyte oxidation on the operating voltage of the battery system.

#### 4. Conclusion

The purpose of this paper was to report the results of a study on the role and effects of gamma-ray irradiation and soybean oil on the properties of a nanoporous HDPE membrane.

The pore volume of the nanoporous HDPE membranes with soybean oil was affected by the extracted amount of oil. Consequently, the pore volume and ionic conductivity of the nanoporous HDPE membranes increased when the content of the soybean oil was increased. The tensile strength of the membrane increased with an increase in absorbed dose of up to 60 kGy, but decreased at 80 kGy due to severe degradation. Finally, the electrochemical stability of the HDPE membrane increased with an increase in absorbed dose of up to 60 kGy.

#### Acknowledgments

This work was supported by Nuclear R&D program through Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology, Korea.

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