Improvement in the Safety of Polyethylene/Montmorillonite Composite Separator for Lithium-Ion Batteries by Electron Irradiation

Sung Woo Kim, Sung Oh Cho*

Department of Nuclear and Quantum Engineering, KAIST, Daejeon, 34141, Republic of Korea Sungwookim98@kaist.ac.kr

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1. Introduction

The separator is a fundamental component of a lithium-ion battery, along with the anode, cathode, and electrolyte, playing a crucial role in safety [1]. It prevents direct contact between the anode and cathode, preventing short circuits, while maintaining a porous structure to facilitate the movement of lithium ions between the electrodes. Additionally, it serves to shut down the battery at temperatures before thermal runaway occurs, providing protection against potential fires. Therefore, the materials used in separators must possess chemical, physical, and thermal stability, while also allowing ion passage through a microporous membrane [2]. Meeting these criteria, polymers are currently the most widely used materials for separators, with commercially affordable polyethylene and polypropylene being the predominant choices.

Despite the use of such materials, safety issues related to battery fires have been a persistent concern for several years. Among the causes of battery fires, the separator plays a significant role, with the risk of the separator being punctured by lithium dendrites that grow from the cathode during the battery charging and discharging process. Additionally, there is a possibility of a sudden increase in temperature or the occurrence of defects in other parts of the battery leading to overheating. Conventional polymer separators exhibit significant shrinkage at temperatures around 130-140 degrees Celsius. It can result in separator damage, leading to short circuits and thermal runaway [3].

To address this issue, there is a type of separator known as a polymer-nanofiller composite separator. It involves blending a polymer separator with mechanically and thermally advantageous filler materials to enhance the stability and performance of the separator. However, merely blending filler materials is not sufficient to achieve these enhanced properties. Fillers tend to agglomerate within the polymer matrix, especially when their surfaces are hydrophilic, and they do not disperse well. Additionally, the adhesion between the polymer and the filler is often insufficient, leading to poor transmission of the properties of filler into the polymer matrix [4].

In this study, particles with a 1-D structure rather than nanoparticles were used as fillers. 1-D structure particles have a larger surface area compared to 0-D nanoparticles, thereby providing more crosslinking sites when observed under an electron beam. Additionally, among the types of fillers, 1-D structure particles are known to have the highest mechanical reinforcement effect. Montmorillonite (MMT) was chosen as one of these particles. MMT is a natural layered clay material, with each layer consisting of two Si-O tetrahedral sheets and one Al-O octahedral sheet. When introduced into the polymer matrix, MMT serves as a 1-D filler with a length of several hundred nanometers. Through the reaction with surface modifiers like silane coupling agents, enhanced dispersion and a larger surface area can be achieved. To enhance the dispersion of MMT within the polymer matrix, a strong hydrophobic silane coupling agent, octadecyl-trimethoxy silane (ODS), was employed for surface modification. Finally, through electron beam examination, the interfacial adhesion between the filler and polymer matrix was strengthened.

2. Materials and Methods

2.1. Materials

The HDPE powder (VH035) employed in this study was commercially manufactured by Korea Petrochemical Co. BNPs with a grain size of 20 nm were acquired from MTI, Korea. ODS was purchased from Sigma-Aldrich. Paraffin oil, hexadecane, and dichloromethane were purchased from Daejung Chemical & Metals Co. Liquid electrolyte, LiPF6 in ethylene carbonate and ethyl methyl carbonate was obtained from Donghwa Electrolyte Co.

2.2 Methods

The silane surface treatment induced the hydrolysis reaction of the silane itself, creating hydroxyl groups. Subsequently, it facilitated the condensation reaction between the hydroxyl groups of each MMT and silane. To induce the hydrolysis reaction of silane, 3mL of ODS was mixed with 25 mL of distilled water in 250 mL of ethanol at 100 °C for few minutes. Immediately after that, to induce the coupling reaction, 10 g of MMT was added and mixed for another 12 h. Subsequently, the mixture was centrifuged to remove reaction by-products other than particles. For impurity removal, ethanol was added, and the mixture was centrifuged

again. The obtained particles were dried at 100 °C for 12 h to obtain particles in powder form.

Surface-treated MMT, HDPE powder, and paraffin oil for use as a matrix were uniformly mixed at 100 °C and processed using a biaxial extruder (BA-11; Bautek Co.) to produce a gel film. In this process, MMT and HDPE mixture along with paraffin oil were added at a weight ratio of 3:7, and the proportion of MMT in the MMT and HDPE mixture was adjusted to 1, 3, 5, and 7 wt.%. The film thus obtained was stretched 5 times in the MD direction and 5.5 times in the TD direction. The stretched film was placed in dichloromethane for approximately 15-20 minutes, and then sonicated very briefly for about 2-3 seconds to remove the paraffin oil inside the film and create a nanoporous structure (Figure 2-4). Subsequently, the sample was subjected to a heat-setting process at 128 °C for 1 min to enhance its thermal and physical properties before the polymer melted. Finally, electron irradiation with an energy of 1 MeV beam was conducted until 100 kGy of doses stacked in air atmosphere. To maintain a constant dose, the membrane was flipped to expose both sides to the electron beam during inspection.

3. Results and Discussion

3.1. Silane surface treatment of MMT

First, the properties of MMT after silane surface treatment were measured. When the untreated MMT was dropped into water, it exhibited hydrophilicity due to hydroxyl groups on the surface, causing it to mix with water and form a slurry. In contrast, the silanetreated MMT, with alkyl groups from silane on the surface, displayed strong hydrophobicity, preventing it from mixing with water and allowing it to float on the water.

To further clarify the chemical structure changes, FTIR absorption spectra were examined (Figure 1). In pure MMT, peaks related to Si, O, and Al were observed; a peak for Si-O-Si stretching at 1035 cm⁻¹, a peak for Al-O-Al stretching at 915 cm⁻¹, and a peak for Si-O plane bending at 529 cm⁻¹. The alkyl groups in ODS/MMT have a structure similar to HDPE, which results in higher dispersibility within the HDPE matrix compared to untreated MMT.

3.2. Safety of separator

To assess the mechanical and thermal stability of the separator, puncture strength and thermal shrinkage were evaluated (Figure 2,3). Puncture strength measurements were conducted on HDPE bare, and samples with 1, 3, 5, and 7 wt.% MMT before and after electron beam irradiation. Prior to surface treatment, the puncture strength values for HDPE bare, 1, 3, 5, and 7 wt.% samples were 0.338, 0.304, 0.348, 0.315, and 0.271 N μ m⁻¹, respectively. Following electron beam irradiation, the puncture strength values for HDPE bare, 1, 3, 5, and

7 wt.% samples were measured as 0.384, 0.36, 0.411, 0.381, and 0.308 N μ m⁻¹, respectively. Only the 3 wt.% sample exhibited higher puncture strength compared to HDPE bare, and the trend of puncture strength was observed as 3, bare, 5, 1, 7 wt.%. For ODS/MMT samples after surface treatment, the puncture strength values before electron beam irradiation were measured as 0.366, 0.449, 0.398, 0.318 N μ m⁻¹ for 1, 3, 5, 7 wt.% samples, respectively. After electron beam irradiation, the values were 0.426, 0.520, 0.460, 0.358 N μ m⁻¹, respectively. Due to the enhanced dispersion caused by surface treatment, all samples after surface treatment showed higher values compared to the untreated samples.

To evaluate the thermal stability, the measurement of the thermal shrinkage was conducted for HDPE bare, 1, 3, 5, 7 wt.% MMT samples. In the case before surface treatment, the measured values for HDPE bare, 1, 3, 5, 7 wt.% samples before electron beam irradiation were 54.5, 51.40, 42.4, 53.3, 59.1%, respectively. After electron beam irradiation, the values were 40.2, 43.9, 36.7, 39.8, 46.3%, respectively. Similar to puncture strength, the 3 wt.% sample exhibited the best thermal stability, and the trend was 3, 5, bare, 1, 7 wt.% in order of better thermal stability. After surface treatment, the thermal shrinkage measurements for 1, 3, 5, 7 wt.% samples before electron beam irradiation were 40.1, 33.7, 44.0, 50.3%, respectively. After electron beam irradiation, the values were 35.5, 21.4, 29.6, 40.6%, respectively. Similar to puncture strength, both surface treatment and electron beam irradiation enhanced the thermal stability, especially for the 3 wt.% ODS/MMT sample, which showed a significant decrease in thermal shrinkage by 33%, reducing from 54.4% of untreated HDPE bare sample to 21.4%. In the evaluation of thermal shrinkage, as with puncture strength, the enhancement effects of characteristics due to surface treatment and electron beam irradiation were clearly confirmed.



Figure 1. FTIR analysis of MMT powder.



Figure 2. Puncture strength of separator, (a) MMT, (b) ODS/MMT.



Figure 3. Heat shrinkage of separator, (a) MMT, (b) ODS/MMT.

4. Conclusion

In this study, a stability- and performance-enhanced MMT-HDPE nanocomposite was fabricated through silane surface treatment and electron irradiation. The MMT particles were uniformly dispersed in the HDPE matrix via a silane coupling agent. Electron irradiation induced cross-linking between polymer chains as well as between polymer chains and silane functional groups. As a result, both mechanical and thermal stability were successfully enhanced. Through various dispersion analyses, it was confirmed that a membrane with a 3 wt.% MMT content exhibited the best characteristics.

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