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Boehmite/Polyethylene Hybrid Nanocomposite Separator Crosslinked by Electron Irradiation for Lithium-Ion Batteries

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1. Introduction

The lithium-ion batteries (LIBs) are rechargeable energy sources for various electronics from small devices such as smart phones or watches to large scale devices including batteries for electric vehicles or energy storage system. As green policies are attracting attention world widely, the demand for LIBs, mainly for electric vehicle to replace internal combustion engines, have been increasing exponentially and is expected to continue to increase in the future. Since modern people live with electronic devices most of the time, battery explosion accidents of smartphones or electric vehicles have always been serious concerns. The battery separator which is one of the four major components of LIBs is responsible for battery safety.[1] The separator is a thin porous insulator that allows lithium ions transportation between the positive and negative electrodes while preventing physical contact each other. The failure of separator can be induced by thermal or mechanical damage. It directly leads to internal short circuits and thermal runaway, which can eventually induce explosions.[2] Therefore, its integrity is the most important factor for the safety.

Various endeavors have been made to enhance the safety of battery. Coating ceramic nanoparticles (NPs) on commercial separators is a representative example to enhance thermal and mechanical properties. Ceramic coated separators (CCSs) show improved thermal stability and mechanical strength compared to conventional separators.[3][4] Although the coating technique have been successful in improving safety of battery by introducing thermally and mechanically outstanding ceramic NPs, it has some drawbacks due to the imperfect adhesiveness.[5] Deficient adhesive strength of the coated layer may induce generation of defects by being peeled off, especially when utilized in curved shaped batteries such as rolled cylindrical or folded prismatic types. In addition, uneven coating layer provides inhomogeneous ion flux while battery is working, potentially causing lithium dendrite on electrodes. Lithium dendrite which can mechanically penetrate or tear separators is one of main mechanical cause of separator failure and should be avoided.

Here, we propose a novel route to fabricating safety enhanced hybrid nanocomposite separators. Boehmite NPs that have thermally and mechanically outstanding properties are homogeneously filled and entangled in the high density polyethylene (HDPE) separator. Boehmite/HDPE hybrid nanocomposite separators crosslinked by electron irradiation have both advantages of inorganic material (thermal and mechanical stabilities) and organic polymer (flexibility and processability). Meanwhile, in nanocomposites, the bonding between nanofiller and the polymer is important; weakly or un- bonded nanofiller may act as an impurity, having the nanocomposites deteriorate properties. We successfully prepared a safety enhanced separator by crosslinking between the silane-treated boehmite NPs and HDPE using electron irradiation.

2. Methods and Results

2.1 Materials

Al wires (99.999%, Sigma-Aldrich) with a diameter of 1 mm were used as the anode. Potassium chloride (KCl) (≥ 99.0%, Sigma-Aldrich). HDPE powder (VH035) used in this work were commercial grades produced by Korea Petrochemical Co., Ltd. (Korea). Various silanes of which functional groups are hydrocarbons with different chain lengths were purchased from Sigma Aldrich (USA): trimethoxy methyl (C1), octyl (C8), and octadecyl (C18) silane. Paraffin oil and n-hexane with extra pure grades were purchased from Daejung Chemical & Metals Co. Ltd. (Korea).

2.2 Preparation of Boehmite NPs

Boehmite NPs were prepared by exactly same way with our previous study. [] As-anodized boehmite NPs are then silane treated to have carbonaceous surface. Hydrocarbon groups in the surface of NPs have better affinity with HDPE and serve as the base to be crosslinked with HDPE by electron irradiation.

2.3 Preparation of Boehmite/HDPE Nanocomposite Separators

The overall process to prepare nanocomposite separator is depicted in Fig. 1. The process consist of (1) extrusion, (2) stretching, (3) oil extraction, and (4) heat setting. Boehmite NPs, HDPE powders, and paraffin oil are homogeneously stirred in one tank at 80℃ and used as raw materials. The composition of the raw materials of boehmite NPs, HDPE, and paraffin oil is 2.5, 27.5, 70 wt% respectively. Gel film is extruded in BA-11 twin extruder (Bautek Co., Korea) with the die temperature of 220℃. The extruded gel film is then sequentially stretched in machine direction (MD) and transverse direction (TD) at 105℃. Afterwards, paraffin oil in the gel film will be extracted in the n-hexane to form pores and heat setting process is implemented at 125℃ for 3 min.

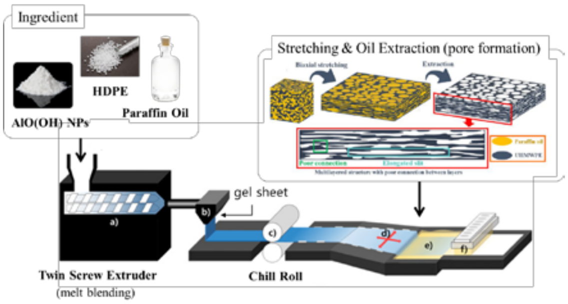

Fig. 1. Schematic illustration of the overall fabrication process

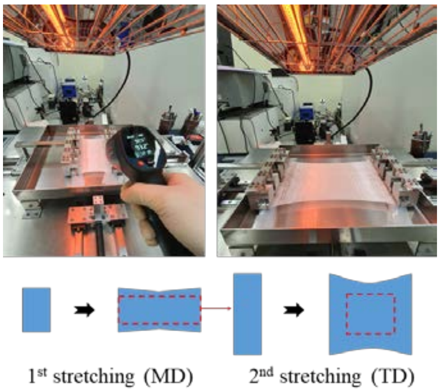

Fig. 2. Sequential biaxial stretching process

2.4 Electron Irradiation

The irradiation procedures were conducted at dose of 200 kGy with the dose rate of 12.5 kGy/pass. The energy of electron was 1.13 MeV. Separators were prepared by stacking them to a thickness of 0.6 mm for irradiation, and thin HDPE films were covered on top and bottom for the uniform dose. The irradiation were implemented upside and bottom side alternatively.

2.5 Measurements

Thermal shrinkage tests were measured in an oven at different temperatures. The thermal shrinkage (S) was calculated by the following equation:

$$S\ (\%) = (A_i - A_f)/A_i * 100$$

where A_i is the initial area of the separators before heating and A_f is the final area of the separators after exposure of the heat.

Mechanical properties of the separators were measured by tensile strength using a universal testing machine, Instron 5848 (Instron, USA).

3. Results

SEM images of Bare HDPE separator and nanocomposite separators with as-anodized, C1-treated, C8-treated, and C-18-treated boehmite NPs are shown in Fig. 3. Boehmite NPs with silane treatment have hydrophobic hydrocarbon surface and the evidences are shown in the FTIR results in Fig. 4.

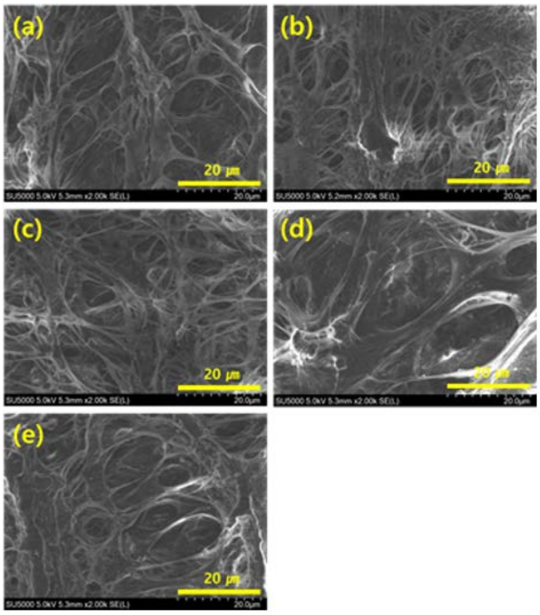

Fig. 3. SEM images of the boehmite/HDPE. (a) bare HDPE separator and (b) as-anodized boehmite, (c-e) C1, C8, C18 silane treated boehmite contained nanocomposite separators.

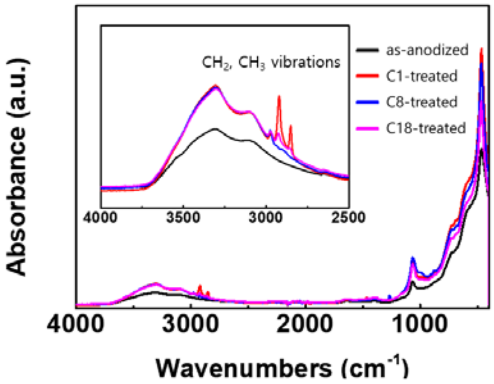

Fig. 4. FTIR spectra of the silane treated boehmite NPs.

Thermal shrinkage test results are shown in Fig. 5. The general requirement in thermal shrinkage for separators is less than 5% at 90℃ for 60 min. All nanocomposite separators surpassed the requirement. Bare HDPE separator and separators with as-anodized, C1, C8, and C18-treated boehmite show thermal shrinkage rate of 36, 34, 26, 24, and 25 % at 130℃ for 30 min while the shrinkage rate of commercial PE separator is 89%. Electron irradiated at the dose of 200 kGy separators of each show even great thermal properties; 21, 19, 18, 17, and 17 % of shrinkage at 130℃respectively under the same conditions.

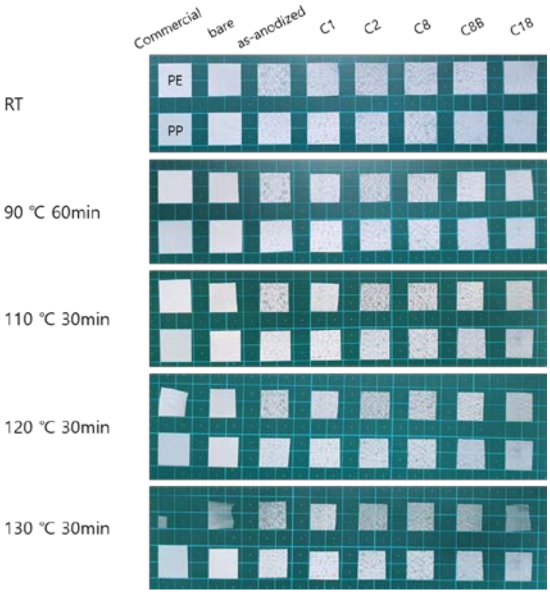

Fig. 5. Tensile strength of the nanocomposite separators.

Tensile strength of the nanocomposite separators also show outstanding results. Fig. 6 shows the tensile results of pristine nanocomposite separators. The results of electron irradiated separators will be analyzed in the future work.

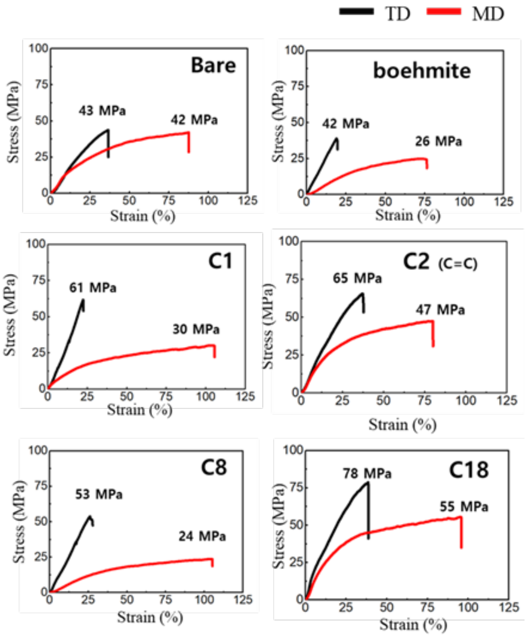

Fig. 6. Tensile strength of the nanocomposite separators.

3. Conclusions

There is a need for a safety-enhanced separator that overcomes the shortcomings of the currently commercialized separator. Preliminary boehmite/HDPE nanocomposite separators has been successfully fabricated. The results show enhanced thermal and mechanical strength compared with a commercial separator. Further study should be analyzed such as DSC, TGA, TMA, and cell tests.

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