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Improvement in the Thermal Properties of Polyethylene/Boehmite Separator for Lithium-Ion Batteries Irradiated by Electron

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1. Introduction

Demand of Lithium ion batteries is increasing every day. Lithium ion batteries are used for mobile phone batteries, electric cars, Energy storage systems, or any other many devices. One of the important parts for Lithium ion battery is separator. Separator has many roles in Lithium ion battery. It separates cathode and anode to prevent short circuit, provide small pores, which Lithium ions can move between the electrodes, and shutdown at the temperature lower than thermal runaway occurs. To satisfy these conditions, material choice for separator is also important. It should have chemical, mechanical, thermal stability. It should block electric current, and have microporous that ion can go through. Therefore, the most common material for separator is polymer, such as polyethylene and polypropylene.

However, there are some safety issue for polymer separator. It is common news that the battery for mobile phone or electric car burns. The number of electric car fire accident in Korea between 2017 to 2020, total 69 fire accidents occurred, 40 of them caused by electrical issue. Thermal defect of separator is one of the main safety issue for battery accident. For example, temperature of a car dashboard is high, especially on a hot summer day or in low latitudes. Overcharging and overheating cause heat shrinkage of polymer that can induce broken of separator and short circuit. If this problem does not be solved, temperature arise can induce the breakdown of separator which causes thermal runaway.

To cover these thermal defects of polymer separator, ceramic nanoparticle addition and electron irradiation were applied to polymer. By mixing ceramic nanoparticles into polymer, it is expected that ceramic particle gives its high thermal resistance property to polymer. Electron beam irradiation gives cross-linking between polymer and polymer. By these new bonding, it is possible to enhance property of separator.

2. Materials and Methods

2.1 Materials

Polyethylene(PE) and boehmite are used for polymer and ceramic. PE/boehmite nanocomposite material was made by twin-screw extruder system. Electron beam irradiation proceeded by Ebtech accelerator, with 100kGy and 200kGy.

2.2 Heat Shrinkage

Make specimen to three by three square, and hold it on the heater on 160 degrees, 30minutes.

2.3 Meltdown Temperature Measurement

Load is applied to specimen and hanged on into the oven. To make same stress for each specimen, width is determined by the simple calculation [1]. Specimen heated 2~3 degree per minute, and check the temperature that the specimen breaks up.

3. Results and Discussion

In case of heat shrinkage, results are shown in figure 3.1 and figure 3.2. It can be easily checked that electron irradiation made strong heat shrinkage resistance for each PE and PE/boehmite case. Square shape preserved in all irradiated specimen cases. In addition, irradiated PE/boehmite shrinks less than PE. Non-irradiated specimens showed random shrinkage rate with many folded patterns. Average heat shrinkage rate in figure 3.2 shows that the shrinkage rate of PE/boehmite is lower than PE, but it is not clear because deviation is too big for each cases. Important point in this experiment is that electron irradiation prevent heat shrinkage sucessfully, and Irradiated PE/ boehmite is better than others.

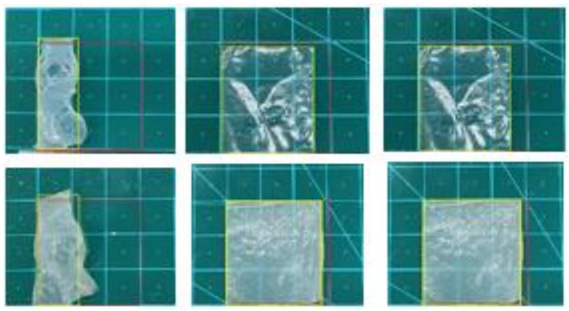

Fig. 1. Heat shrinkage result of PE, PE-100kGy, PE-200kGy, PE/boehmite, PE/ boehmite-100kGy, PE/boehmite-200kGy.

For meltdown temperature, Figure 3.3 shows the result for each cases. As expected, electron irradiation increases the meltdown temperature. Irradiated PE/boehmite shows high meltdown temperature than PE, and higher dose make higher meltdown temperature. It is same result with heat shrinkage experiment.

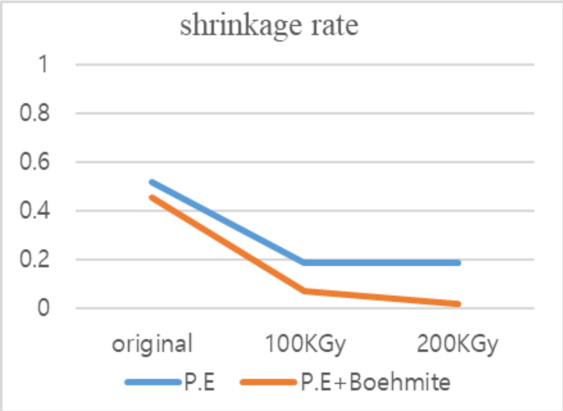

Fig. 2. Average heat shrinkage rate of PE and PE/boehmite.

However, one thing is that not irradiated PE/boehmite shows very low PE/boehmite temperature than expected. Experiment repeated again with changing width, load, or to new film for PE/boehmite, but still temperature was abnormally lower than others.

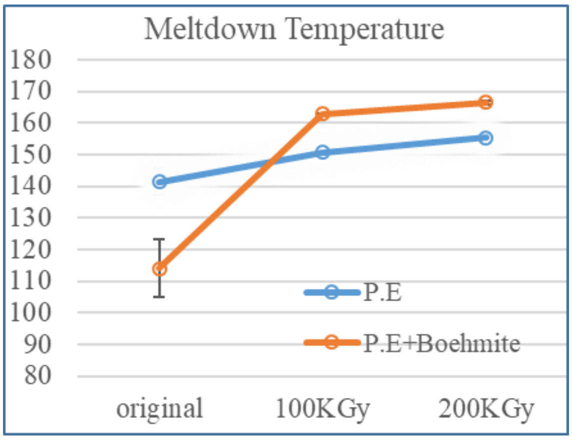

Fig. 3. Meltdown temperature of PE and PE/boehmite before and after electron radiation.

To analyze these results, two more test applied. First one is boiling xylene test. By measuring weight percentage of the remaining gel after long time, it is possible to measure cross-linking rate. Figure 3.4 shows that gel content rate is higher in 200kGy than 100kGy, which means high dose makes many cross-links.

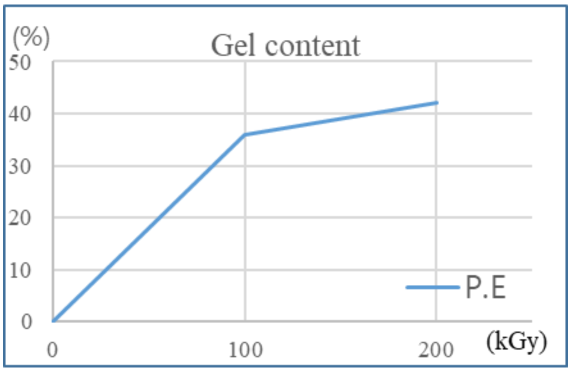

Fig. 4. Gel content of PE by different irradiation.

FTIR absorbance test also applied. Peaks shown in figure 3.5 means the absorbance of bonding between atoms. Important point is ≈1716 〖cm〗^(-1). Only irradiated PE has this peak, and it shows the absorbance of carbon -oxygen double bond. By this result, we can know electron irradiation induces double bond between carbon and oxygen in PE, and it binds with hydrogen of boehmite to make hydrogen bonding. It is strong bond to enhance properties.

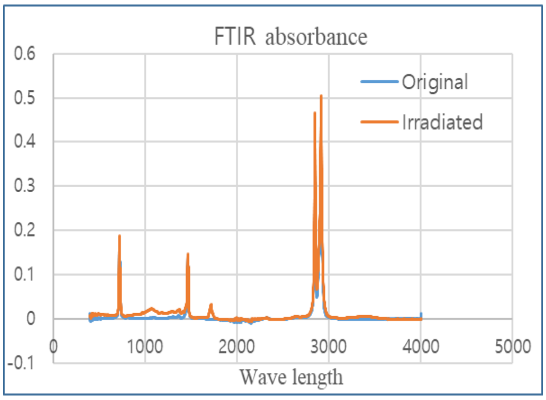

Fig. 5. Absorbance of PE before and after electron irradiation.

To explain what happens to the meltdown temperature, figure 3.6 was attached. Original PE has no crosslink, so it is broken at the proper temperature. Irradiated PE has many crosslinks, which tends to maintain its own shape. For original PE/boehmite, boehmite is hydrophilic because it has many hydroxyl group, and PE is hydrophobic, so maybe this can affect to thermal property of PE/boehmite. Finally, irradiated PE/ boehmite has both crosslink between polymer and hydrogen bonding, so it shows the best enhanced thermal property.

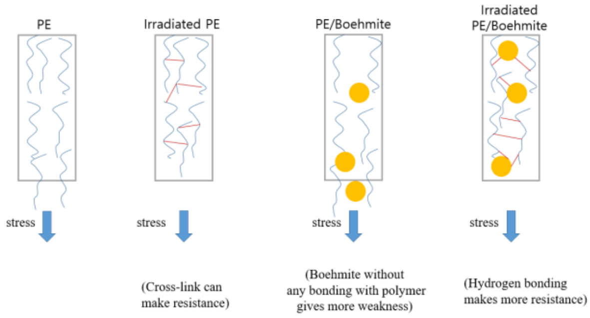

Fig. 6. Expected picture as temperature increases for each cases.

4. Conclusion

Heat shrinkage protection, and making gap between melting temperature and shutdown temperature by irradiation was successful. Thermal properties are enhanced better as electron dose increased. However, Meltdown temperature of not irradiated PE/boehmite should be rechecked. Electron irradiation is essential for it.

REFERENCES

[1] Hyungu Im et al., "Improvement of Thermal Stability of Polyethylene Lihium-Ion Battery Separator via Coating with Polymers Synthesized from Bis-GMA Derivatives", Polymer(Korea), Vol. 34, No. 6, pp 517-521, 2010