Curable Polymeric Binder/Ceramic Composite-coated Superior Heat-resistant Polyethylene Separator for Lithium Ion Batteries†

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A thermally stable modified PE separator prepared as a necessary component of lithium-ion batteries (LIB) for electric vehicle (EV) by coating the composite of curable copolyester (cPET) and Al2O3 onto the surface of bare polyethylene (PE) separator. After curing, the composite-coated separator demonstrated excellent dimensional stability at high temperature. Even when exposed at 170 °C, the composite-coated separator shrank only 13% and the unit cells containing the cPET-PE separator performed cycle life almost close to that of cells made from bare PE separator.

Nowadays, lithium-ion batteries (LIB) become the most important electrical power sources because of their high power, capacity, and energy density as well as excellent cycle life;1-4 thus, the demands for LIB have increased remarkably in many industrial areas. Inevitable needs for electric vehicle (EV) lead to the ever growing demands for LIB since it has been considered as the most promising candidate which meets both power and energy capabilities required for EV. Many researches have devoted their efforts to improve the performances of LIB such as power capability, energy density, and heat stability. Regarding the power capability and energy density, active materials employed in electrodes are dominantly contributing factors, thus most of studies related to the enhancement of LIB performances have focused on the development of high power capacity materials for cathode5-8 and anode.9,12 However, particularly in the field of EV application, the heat stability of separator is and will be a key issue to govern the safety of whole EV because huge amount of heat is generated from the EV batteries which are equipped with high power energy devices.13,14 There are two main heat generating sources;14 one is the increased length between the current source and the tab and the other is the current concentrated near the tabs.

The separator physically isolates the cathode and the anode so that the possibility of an internal short-circuit, which may cause explosion,15-20 is reduced and prevented in more desirable manners. Currently, the separator based on polyethylene (PE) or its family is dominantly employed for almost of LIB because its mechanical and thermal shutdown properties, electrochemical stability, low cost, and established commercial fabrication are well examined and confirmed compared to other competitive materials.21,22 Nevertheless, the PE separator has two major defects; low wettability toward the electrolyte and heat instability resulted from its intrinsic polymer chain structure. Because PE is composed of hydrophobic hydrocarbons, the wettability of the electrolyte, which is generally consisted of hydrophilic liquid species, is very poor and results in low ion conductivity. Other competitors derived from hydrophobic polymers like polypropylene are not much better regarding to this aspect. Not only the modification of base separator materials but also the various surface treatments have been attempted to solve this problem. Between two methods, the latter is believed to be more effective in the practical viewpoint. Grafting, irradiation, and coating of hydrophilic components onto the bare hydrophobic separator surface have been proven to increase wettability.23-28 As an one example, treating the PE separator with polydopamine has been found to be very effective for increasing the power capability.26-28

Heat instability is a more significant defect for the PE based separator. When the temperature goes up above 120 °C, the PE separator starts to shrink (Fig. S1, In the ESI†) and may lead to fatal damage during actual device operation. In order to apply LIB for EV without anticipating this problem, the thermal dimensional stability of the separator should be retained at high operation temperatures of LIB. However, any other approach to replace the PE separator by other polymer derived separators seems to be not plausible practically.29,30 Instead, coating the surface of PE separator with more thermally stable material has been taken into consideration as an alternative. To classify various approaches carried out in this context, there are two different methods available in the literatures (Table S1, In the ESI†). One is to coat the PE separator with high temperature polymer like polyimide.32 The other is to apply the polymer/ceramic composite as physically supporting layers for diminishing the shrinkage of the bare PE separator.33-35 When considering the effectiveness, the former method is profoundly inferior than the latter. Therefore, the composite is cast onto the PE separator from the solution mixture of thermoplastic polymeric material and ceramic filler, typically Al2O3, followed by solvent evaporation to produce the composite film layers which are thin enough not to deteriorate the electrolyte transfer but robust to hold the PE separator strongly enough. Since the main role of polymeric material is to bind the ceramic particles together, it is usually referred to as binder. Considering that the melting temperature (Tm) of PE itself is around 140 °C, abrupt shrinking of PE separator around Tm of PE is inevitable. To date, coating of ceramic composite which is the mixture of
polyvinylidene fluoride (PVdF) and Al₂O₃ has been proven to be the most effective method to enhance heat stability of PE separator. However, heat stability of PVdF/ceramic composite-coated PE separator cannot exceed the Tₘ of PVdF itself. Comprehensive literature survey on the shrinkage of composite-coated PE separator reveals that the shrinkage reduces from >80% to <10% when exposed at 150 °C for 1 h (Table S1, In the ESI†). Surprisingly, very few approach has been attempted to apply a thermosetting binder. In general, thermosetting system builds crosslinked network structure after crosslinking (or curing), then both heat stability and chemical resistance are expected at the same time, which is the main idea of this study. Among a variety of thermosetting binders, very limited numbers of species can be considered for the coating material on PE separator. The curing temperature should not exceed 100 °C, at which temperature the heat shrinkage of PE separator begins. The material employed in this study satisfies that requirement.

We suggest copolyester based curable system as a novel polymeric binder for ceramic composite-coated PE separator. Generally, copolysteres are typically produced from near-equimolar reaction between diacid like terephthalic acid and diol like ethylene glycol. Copolysteres are made by incorporating additional third or more comonomers; typically diacids such as isophthalic acid and diols such as cyclohexane dimethanol. Through proper combination of main monomers and supplementary comonomers, variety of many copolysteres having diverse thermal properties, adhesion properties, toughness, chemical resistance, clarity, and color stability can be manufactured through well-controlled molecular architecture design. Moreover, copolysteres can be crosslinkable by reacting further with various crosslinkers such as isocyanates, melamines, or epoxies since more than two hydroxyl groups can be incorporated in copolysteres. Among the crosslinkers, isocyanates are presumed to be the most suitable for coating the PE separators because the curing reaction between the hydroxyl groups in copolysteres and the isocyanate groups in crosslinkers is able to occur at the temperature lower than 100 °C, which would not impose any shrinkage of PE separator sandwiched between two binder/ceramic composite layers. Once appropriate crosslinking is achieved, enhanced heat stability is expected as schematically shown in Scheme 1.

In this paper, copolysteres (cPET) are introduced as a novel polymeric binder for ceramic composite-coated PE separator. To examine this idea, various cPETs of commercial sources were employed and the crosslinkable system based on them was designed and subsequently the composite of cPET and Al₂O₃ was coated onto the surface of bare PE separator and cured, then the thermal and electrochemical properties were evaluated.

Firstly, the intrinsic dimensional stability of bare cPET film after curing at high temperatures were compared with bare PVdF film to evaluate the heat stability when applied as a binder. The concentration of crosslinker was 4 equivalents to the hydroxyl value in cPET; cured cPET was not dissolved out in tetrahydrofuran (THF) whose solubility toward cPET is much better than electrolyte when the amount of crosslinker exceeds 4 equivalents (Fig. S2, In the ESI†). Cured cPET and PVdF films with a thickness of 50 μm were exposed at two different temperatures of 150 and 200 °C, respectively, for 1 hour under vacuum. After 1 hour exposure, the PVdF film shrunk 16% at 150 °C and 24% at 200 °C (Fig. 1). The intrinsic crystalline nature of PVdF molecule caused shrinkage at high temperature, Tₘ of PVdF was found to be 148.9 °C measured by DSC (Fig. S3, In the ESI†). Moreover, the edges of the PVdF film were significantly damaged, indicating that the thermoplastic PVdF is not thermally stable above its Tₘ. This clearly demonstrates the pivotal limitation of thermoplastic PVdF as a high temperature binder material for ceramic composite-coated separator. On the other hand, the cured cPET films showed excellent heat stability under the identical heat exposure conditions. Heat shrinkage percentages of cured cPET films were 6 and 8% at 150 and 200 °C, respectively. As expected, crosslinked network structure of cured cPET gives lower heat shrinkage. In addition, their edges and surfaces were nearly undamaged compared to initial shape. DSC thermograms of cured cPET shows no distinct melting peak, meaning that it is completely amorphous. Therefore, it was possible to maintain its dimensional shape even at a temperature higher than 150 °C in spite that it is amorphous. Discussing the thermal degradation under nitrogen conditions, PVdF and cPET started to decompose at 430 and 390 °C, respectively (Fig. S4, In the ESI†). The initial decomposition temperature of the PVdF was slightly higher than that of the cPET. However, when considering the operating temperature of actual LIB, 390 °C is a
quite sufficiently high temperature to certify the heat stability. The word, ‘heat stability’, used in this study means the resistance to heat shrinkage rather than the thermal decomposition. The heat shrinkage is much more important factor in the batteries since the material is used at the temperature quite lower than its decomposition temperature. The TGA curves support that the cPET binder is thermally stable enough when considering the operation temperature of the batteries. From these results, it is concluded that the crosslinkable cPET has very desirable thermal properties as a curable binder for composite-coated LIB separator.

Secondly, in order to evaluate the high temperature performance of the cPET as a binder the mixture of cPET and Al₂O₃ dissolved in specific solvent mixture was coated onto the surface of bare PE separator and subsequently cured at 100 °C for 1 min and the thermal properties of the cPET/Al₂O₃ composite-coated PE separator, which will be referred to as cPET-PE afterwards, were analyzed. The molecular weights of uncured cPETs are definitely very low compared to typical polymeric materials. Therefore, no anchoring effect of cPET into the pores existing in PE separator is expected and phase separation was usually observed. Co-solvent was found to be effective in reducing this phase separation phenomenon (Fig. S5, Fig. S6, and Table S2, In the ESI†). The surface and cross sectional SEM images of the PE separator coated by cPET/Al₂O₃ composites are shown in Fig. S7a and b, In the ESI†. In Fig. S6a, Al₂O₃ particles were uniformly dispersed throughout the separator surface. Generally, the binder plays a role of connecting the inorganic particles to maintain a fixed shape. In the cross sectional view, the cPET/Al₂O₃ composites were coated very thinly onto both sides of the PE separator. The thicknesses of the PE separator and single cPET/Al₂O₃ composite layer were 9 and 3 μm, respectively (Fig. S7b, In the ESI†). The total thickness of the cPET-PE separator was 15 μm, which is thinner than or similar to that of non-coated PE separator commercially available. To ensure good lithium ion movement, it would be beneficial to have a thin coating layer when applying ceramic composite-coated separator for LIB. The overall thickness of the cPET-PE separator obtained in this study was thin enough to expect sufficient ion conducting ability.

Fig. 2 shows the heat shrinkage experiments results for bare PE and cPET-PE separators. Non-coated bare PE separator shrank 25% at 130 °C, whose temperature is close to the Tₘ of PE itself and shrank more than 70% at temperatures above 130 °C. Because the Tₘ of PE material was found to be 140.1 °C (Fig. S3, In the ESI†), the PE separator, which is manufactured through a stretching process to produce the pores desirable for liquid electrolyte transfer, tends to revert to the originally unstretched state. This may cause an internal short-circuit between the cathode and anode. However, cPET-PE separator shrank only 13% even at 170 °C. This low heat shrinkage is very desirable property when applied as LIB separator for EV. The heat shrinkage results indicate that the cPET binder exerts well as a mechanical support to reduce the heat shrinkage of bare PE separator through its crosslinked structure formation. This robust structure was achieved by optimizing the amount of crosslinker (Fig. S8, In the ESI†). Not every copolyesters were successful. According to our experiments results, crosslinking density which corresponds to the average molecular weight between crosslinks and can be determined from the molecular characteristics of cPETs employed in this study. Hydroxyl value and average molecular weight were found to be the most critical factors (Fig. S9 and Table S3, In the ESI†). The results presented in Fig. 2 prove that the cPET-PE separator obtained has tremendous dimensional stability above the Tₘ of PE separator in spite of its extremely thin coating.

Finally, to evaluate the performance of battery containing the cPET-PE separator a battery cycle test was carried out for unit cells and the results were compared with cells made using bare PE separator (Fig. 3). If cPET binder reacts with electrolytes or decomposes within the operating voltage ranges of LIB tested, it would not be possible to obtain the reasonably stable cycle performance shown in Fig. 3. After 50 cycles, the relative discharge capacity of the cells containing the bare PE separator and cPET-PE separator were 88 and 80%, respectively. When comparing coulombic efficiency (Fig. S10, In the ESI†), the cell containing cPET-PE separator showed a little bit lower stable cycle property compared to the cell containing bare PE separator and this might be one of the reasons causing the reduction of
discharge capacity. Although the capacity of cPET-PE separator-containing cell is a little bit lower than that of the bare PE separator-containing cell, no undesirable abnormal cycle test results which can be considered as unstable battery operation were observed during cycle test, indicating that the crosslinked cPET binder did not induce any harmful reaction that will interrupt normal operation. If the cured cPET does not have a three-dimensionally crosslinked network structure, whole or at least a part of cPET would have been dissolved out in the liquid electrolyte. The resistance against polar compounds used for liquid electrolyte would be additional benefit of the crosslinked structure of cPET. Therefore, it is concluded that the cPET-PE separator-containing cell was able to show stable battery cycle properties.

Battery performance diminishes as the thickness of separator increases and also as the air permeability of separator or the wettability of separator toward the electrolyte decreases. Regarding the thickness and air permeability, the cPET-PE separator has thicker thickness and lower air permeability compared to bare PE separator that will exert as disadvantageous effects on the battery performance. However, in the view of wettability, the cPET-PE separator is more advantageous than bare PE separator since the cPET-PE separator is covered with hydrophilic alumina particles and cPET binder containing hydroxyl groups in its backbone. On the other hand, the surface of uncoated PE separator is intrinsically hydrophobic. The difference is clearly observed from a contact angle measurement with electrolyte liquid (Fig. S11, In the ESI†). Even though cPET is an organic material, unreacted hydroxyl groups present in cPET render more hydrophilicity to cPET binder and the pores existing among the Al₂O₃ particles also have a positive effect on the enhancement of wettability. As a consequence, the cPET-PE separator has the potential to perform with better battery cycle test results if its air permeability is improved by adjusting the amount of cPET binder in composite and/or optimizing the coating process.

Conclusions

In summary, a thermally stable cPET-PE separator was developed as a necessary component of LIB for EV by coating curable cPET/Al₂O₃ composite onto the surface of bare PE separator. After curing, the cPET-PE separator demonstrated excellent dimensional stability after exposing at high temperature. Even when exposed at 170 °C, the composite-coated separator shrank only 13%. The battery performance of unit cells containing the cPET-PE separator was almost close to that of cells made from bare PE separator despite that addition layers were coated. Considering that cPET is more hydrophilic compared to PE, more improvements in battery performance can be achieved when further systematic studies are carried out.

Experimental section

Copolymers were kindly provided by SK Chemicals, Korea and their molecular characteristics are shown in Table S3, In the ESI†. cPET4 (ES-660) was mainly used for most experiments described in the main text. Polyvinylidene fluoride (Solef® 21216, molecular weight: 600,000 Da) was received from Solvay. The catalyst, dibutyltin dilaurate (DBTL) was purchased from Sigma Aldrich. Isocyanate crosslinker (Desmodur N-3300, hexamethylene diisocyanate trimer type) was supplied from Bayer. Tetrahydrofuran, cyclohexanone, and acetone of reagent grades were purchased from Samchun Chemicals, Korea. Alumina particles (LS-235) with a mean particle size of 500 nm were received from Nippon Light Metals, Japan. The PE separator (ND-509, Asahi Kasei, thickness : 9 μm, air permeability : 160 s/100 cc) was used as a substrate. LiNi₀.₅Co₁.₅Mn₀.₅O₂ (Samsung SDI) and graphite (Samsung SDI) were used as the cathode and anode active material, respectively. The liquid electrolyte used for the experiments was 1 M LiPF₆ in a mixture of 30/70 (v/v) EC/EMC (Solvbrain, Korea).

In order to test the heat stability of bare separator without any filler, 10 wt% PVdF in acetone and 20 wt% cPET in 70/30 (w/w) tetrahydrofuran/cyclohexanone mixture were cast onto poly(tetrafluoroethylene) film and the film test specimens were obtained after solvent removal. In the cPET solution, crosslinker (4 equivalents to hydroxy concentration in cPET) and DBTL (0.5 wt% to sum of cPET and crosslinker) were added. After drying the solvents in the hood overnight, the cPET film was cured in the convection oven at 100 °C for 1 minute. The cured cPET film was aged for post-curing in the convection oven at 50 °C for two days. The PVdF film was prepared without any further treatment after evaporation of acetone.

The cPET/Al₂O₃ (1/7 by wt) composite-coated PE separator (cPET-PE) was fabricated by dipping a bare PE separator in the coating solution followed by solvent evaporation. The coating solution was manufactured by the following steps. Firstly, alumina particles were dispersed in the 70/30 (w/w) tetrahydrofuran/cyclohexanone mixture solvents. Secondly, cPET, crosslinker (4 equivalents to hydroxy concentration in cPET), and DBTL (0.5 wt% to sum of cPET and crosslinker) were added. To prepare the coated films, evaporation of solvent and the curing process were conducted employing the methods identical to those described for the preparation of bare binder film. The air permeability of the obtained cPET-PE separator was 5,000 s/100 cc when measured by a Gurley densometer.

Separators of size 6 cm x 6 cm were marked with two 4 cm lines that crossed in the middle of the separator for the heat stability test. The separators were baked in an oven at each temperature for 10 min (Fig. S12, In the ESI†), and the resulting shrinkage was calculated by measuring the new lengths of the lines. Shrinkage test results given herein were measured in the machine direction.

For the battery cycle life tests, the pouch-type cells were prepared with a size of 5 cm x 6 cm. The separator was located between two electrodes. The amounts of active materials were adjusted to give capacity of 60 mAh for a unit cell. The unit cells were cycled between 3.0 and 4.2 V at a constant current rate of 0.2 and 0.5 C for charging and discharging, respectively.

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Notes and references

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Graphical abstract

A thermally stable cPET-PE separator was developed by coating curable cPET/Al$_2$O$_3$ composite onto the surface of bare PE separator.