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Continued Advancements in Separator Technology Performance

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Abstract

New generation lithium ion battery separators - co-extruded multi-layer separators - were introduced in 2007 by Tonen to improve permeability and thermal properties, targeting the improvement of power and safety. The first generation co-extruded separator designs increased meltdown temperature by 40 ºC. We have continued to advance the co-extruded separator platform targeting further improvements for battery safety. Building on the improvements of the first generation co-extrusion, our most recent advancements reduce separator shrinkage at elevated temperature and lower shutdown temperature. Combined with the higher meltdown temperature of the first generation co-extrusion technology, improved shrinkage and shutdown performance continue to widen the safety margin for lithium ion batteries. The new generation separators are produced using Tonen's proprietary wet fabrication process and co-extrusion of specially tailored polyolefins developed by ExxonMobil Chemical, and are commercially available for advanced HEV/EV and also small electronics lithium ion battery applications.

Keywords: Safety, lithium battery, secondary battery, HEV, EV

1 Introduction

In 1979, Pennings et al. reported gel spinning and super drawing of ultra high molecular weight polyethylene to obtain highly oriented high modulus and high strength filaments[1]. Crystallization from solution reduces entanglement of ultra high molecular weight polyethylene and facilitates extended chain crystal orientation when highly oriented. Kono et al. reported bi-axial orientation of gel sheets of ultra high molecular weight polyolefins, by what is often referred to as the "wet process", to obtain microporous membrane in 1984[2].

Bi-axially oriented thin, strong and microporous polyolefin films provide many advantages as separator for lithium ion batteries[3], [4], [5]. A Tonen polyethylene micro porous film separator was used in the world's first commercial lithium ion battery by Sony in 1991, because it delivered the best balance of battery capacity, power, reliability, and safety. The demand for lithium ion batteries has increased rapidly, and now they are used in cell-phones, laptops, camcorders, digital cameras, and power tools.

The separator must also be chemically inert, uniform and free of flaws. The separator insulates the cathode and anode electrically, while allowing ready ion transport. In addition, the separator should be stable in all its properties within the temperature range of the battery operation for the life of the battery. High strength and low heat shrinkage are required for insulation performance in the solid state to prevent direct contact of anode and cathode. If the battery becomes too hot due to exothermic reaction or external heating under abuse conditions, the separator can work as a fail-safe switch of the ionic transport between electrodes by closing the pores and shutting down the cell circuit. Shutdown is basically observed around the melting point of the material (historically, around 130ºC for polyethylene), and the separator undergoes a solid to melt transition; however, it should maintain its integrity (melt integrity) in order to prevent the direct contact of the electrodes in melt state, until meltdown occurs due to further temperature rise caused by heat liberation. The differential between meltdown temperature and shutdown temperature establishes the safety margin of the separator.

Around 2010, new lithium ion battery applications for hybrid electric vehicle (HEV), plug-in HEV and electronic vehicle (EV) are scheduled. Larger size lithium ion batteries are developing with higher power than existing applications such as cell-phones, laptops, and power tools. Kimishima et al. reported micro structure controlled power related performance of lithium ion batteries in 2006[4]. Moreover co-extruded multi-layer separators were developed to improve thermal integrity as an extension of the proprietary wet process. The high permeability of the separator markedly improved the power of the batteries. And improved thermal integrity contributes to achieve more safety margin of the separator to meet potential needs. The new generation separators are produced using ExxonMobil's advanced technology platform: a union of our proprietary wet fabrication process with co-extrusion of specially tailored polyolefins[5-7]. In this work, we will introduce the new technology to continue adding safety margin for batteries as an extension of our Co-extrusion Separator Technology Platform.

2 Performance of the Advanced Separator for HEV/EV Applications

2.1 Co-extrusion Technology using Specific Tailored Polyolefins

Advanced separator has been produced by co-extrusion technology based on the wet process using specifically tailored polyolefins. Co-extrusion technology can be advantageously combined with the wet process. For HEV/EV applications the primary requirement is high permeability to contribute to high battery power. Generally high permeability could be attained with the high porosity of the separators; however, it often results in reduced strength and thermal integrity. Furthermore thicker separators are generally used with large batteries in order to ensure reliability and safety, which could decrease the permeability as well. Advanced separator produced by co-extrusion of specific polyolefins resolves those contradictions and expands the capability, achieving high permeability (porosity) while improving strength. In addition, co-extrusion of specific tailored polyolefins improves thermal properties such as thermal integrity greatly and should enhance safety performance of batteries.

2.2 Typical Properties of Co-extruded Multi-layer Products

Table 1. Separator properties for commercial Mono/Co-extruded layer separators

		Co-extruded				Mono-layer
Separator Properties		V25CGD	V25EKD	V20CFD	V20EHD	E25MMS
Separator thickness	micron	25	25	20	20	25
Air permeability	sec / 100 ml	180	270	170	290	650
Porosity	%	49	46	43	42	36
Shutdown temperature	^{o}C	134	134	134	134	131
Meltdown temperature	^{o}C	185	185	185	185	155
Heat shrinkage MD (@105 ^{o}C, 8hr)	%	3.5	3.5	3	3	6
Heat shrinkage TD (@105 ^{o}C, 8hr)	%	1.5	1.5	1.5	1	4.5
Heat shrinkage MD (@130 ^{o}C, 0.5hr)	%	15	21	13.5	12	37
Heat shrinkage TD (@130 ^{o}C, 0.5hr)	%	15	22	13	11	35.5
Puncture strength	gf	360	550	280	430	590
Tensile strength MD	kgf/cm^2	700	1100	650	1050	1500
Tensile strength TD	kgf/cm^2	800	1300	750	1300	1300

The typical properties of these new generation commercially available separators (V25EKD, V25CKD, V20CFD, V20EHD) are summarized in Table 1 along with those of a commercially available polyethylene mono-layer separator (E25MMS) [6], [10]. As for the co-extruded multi-layer separator, higher permeability (e.g., low Gurley number) and porosity can be attained against polyethylene mono-layer separator. The properties could be controlled by material design as well as the fabrication condition, giving flexibility of separator performance for each battery design.
Note that the combination of Tonen's co-extrusion wet processing and EMCC's polymer technology results in a separator having generally improved separator performance at elevated temperature.

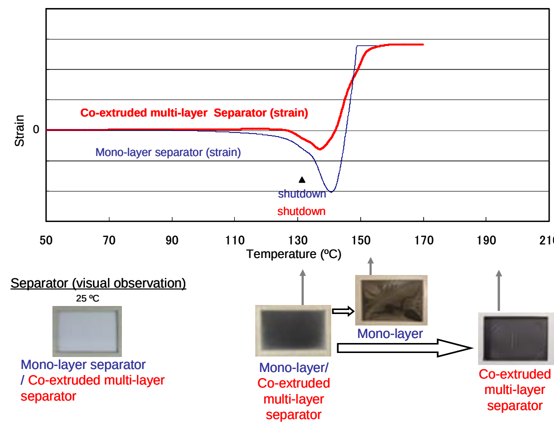

Figure 1. TMA strain and Visual observations for co-extruded multi-layer separator and polyethylene monolayer separator

2.3 Thermal Property of Co-extruded Multi-layer Separator

Thermal mechanical analysis (TMA) is often used for thermal physical performance evaluation. In Figure 1, the TMA strain behavior of a co-extruded multi-layer separator (V25EKD) is shown as a bold line against that of polyethylene monolayer separator (E25MMS) as a thin line[7], [10]. And photos of separators fixed on four sides in a frame are shown also. Both separators show the same visual observation, color change from opaque to transparent, and the same TMA strain behavior up to shutdown temperature, around 130 ºC. Photos show that polyethylene monolayer separator broke over 150 ºC, while co-extruded multi-layer separator maintained its melt integrity with little elongation against strain and did not break up to 190 ºC. Consequently, the safety margin of co-extruded multi-layer separator was about 40 ^{o}C wider than one of polyethylene monolayer sample.
In order to understand the difference in the thermal physical behavior, we investigated the surface structure change of co-extruded multi-layer separators during heating up to 180 ºC by atomic force microscopy (AFM)[10]. When above shutdown temperature, at 140 ºC, some of the networks appear to remain unchanged while bulk domains appear to be embedded in them. This result suggested the remaining networks seemed to act as a skeleton and absorbed molten domains in them, maintaining melt integrity even at 180 ºC. Consequently, co-extruded multi-layer separator improved its melt integrity and should enhance the safety of batteries.

Table 2. Separator properties of new developing grades and commercial grades

Separator Properties		Developing Grades		Co-extruded Commercial Grades		Mono-layer
		Developmental grade 1	Developmental grade 2	V25CGD	V25EKD	E25MMS
Separator thickness	micron	25	25	25	25	25
Air permeability	sec / 100 ml	270	590	180	270	650
Porosity	%	39	38	49	46	36
Shutdown temperature (SDT)	^{o}C	134	**128**	134	134	131
Meltdown temperature (MDT)	^{o}C	185	185	185	185	155
Safety Margin (MDT-SDT)	^{o}C	51	**57**	51	51	24
Heat shrinkage MD (@105 ^{o}C, 8hr)	%	2	6.5	3.5	3.5	6
Heat shrinkage TD (@105 ^{o}C, 8hr)	%	1	3	1.5	1.5	4.5
Heat shrinkage MD (@130 ^{o}C, 30 min.	%	9	31.5	15	21	37
Heat shrinkage TD (@130 ^{o}C, 30 min.)	%	**8**	31	15	22	35.5
Puncture strength	gf	410	490	360	550	590
Tensile strength MD	kgf/cm^2	850	1050	700	1100	1500
Tensile strength TD	kgf/cm^2	1000	1050	800	1300	1300

The temperature dependence of impedance in a small model cell clarified that high impedance is maintained at a high level of over 100,000 ohm-cm^2 up to the upper temperature limit of the equipment, 180 ºC. The impedance result was consistent with the melt integrity and meltdown temperature of separator measured by TMA strain behavior, visual observation and AFM observation.

2.4 Power Improvement of Batteries for High Power Batteries

The permeability and porosity of the separator affect the ionic transport in the electrolyte. And the internal resistance strongly affects the total cell performance under high rate condition. Therefore a highly permeable separator would be required to cope with the recent progress of the electrode performance for HEV/EV lithium ion battery application. Figure 2 shows the result of discharge rate performance tests for a 30Ah laminate EV cell with typical electrodes and electrolyte[10]. The discharge condition was 0.5C-4C and is measured from 4.15~2.90V at 25ºC. The test result of co-extruded multi-layer separator (V25EKD) is shown as bold lines against that of polyethylene mono-layer separator (E25MMS) as thin lines. The co-extruded multi-layer separator showed better discharge performance compared to the polyethylene mono-layer separator especially at high rate condition. This result is consistent with the permeability and porosity of the separators (Table 1).

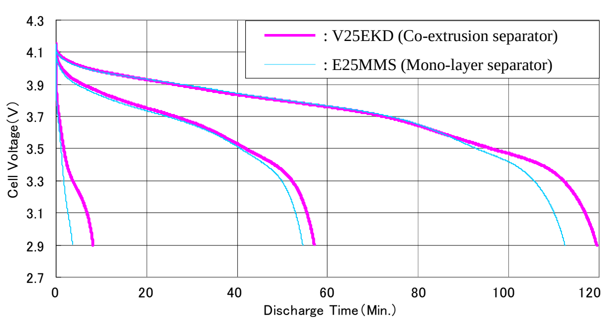

Figure 2. Discharge performance result of co-extruded multi-layer separator and polyethylene mono-layer separator

2.5 Further enhanced thermal stability for larger battery cell

Larger battery cells have been developed for HEV/EV application in contrast to personal electronics application. Thermal stability, i.e. heat shrinkage is more critical for larger battery cells. V20EHD has been developed to improve heat shrinkage in commercial co-extrusion products, V grades. We are devoting our efforts into further improvement of heat shrinkage to meet customers' requirements. New separator developmental grade 1 in Table 2 shows lower heat shrinkage at 130 ^{o}C than our standard commercial mono layer and even latest low heat shrinkage commercial V grade, V20EHD. Reduction of strain of polyolefin crystalline region is the key concept for the improvement of heat shrinkage at high temperature. The developmental grade 1 has lower heat shrinkage at 130 ^{o}C against commercial V grades while heat shrinkage at 105 ^{o}C is roughly the same as V grades. It also possesses good property balance, e.g. good permeability and strength while achieving low heat shrinkage. This low heat shrinkage developing grade expands opportunities to apply ExxonMobil's separators having good mechanical property balance, into large battery cell market.

2.6 Safety enhancement by tailor-made polyolefin in combination with Co-extrusion Technology

Our mono layer separator has good melt integrity around 150 ^{o}C. Melt integrity is one of the safety functions our separator provides. Co-extrusion technology has provided further safety enhancement by improving melt integrity at higher temperature. The melt integrities for commercial co-extrusion grades are over 185 ^{o}C (Table 1). The other key safety function of the separator is shutdown performance. Good shutdown performance stops the current in the battery by melting PE to close pores when the battery becomes too hot under abuse conditions. If shutdown temperature decreases, the current in the battery stops before the temperature rises beyond a catastrophic level. Co-extrusion technology has a possibility to provide wider safety margin, i.e., lower shutdown temperature and higher meltdown temperature. In general, shutdown temperature varies from 130 to 135 ^{o}C in commercial grades. New specially tailored polyolefins developed by ExxonMobil Chemical have enabled us to achieve lower shutdown temperature than commercial grades while retaining other general film properties. Shutdown performance in separators can be defined by two methods, change in permeability at elevated temperature and by measuring changes in impedance in a battery cell.

Shutdown performance of separators was evaluated by permeability change at elevated temperature. The grade we developed has a better shutdown temperature, 128 ^{o}C, which is 6 ^{o}C lower than commercial V grades, while maintaining higher meltdown temperature derived from co-extrusion technology (development 2 in Table 2). Consequently, we have developed a new separator having about 60 ^{o}C of safety margin.

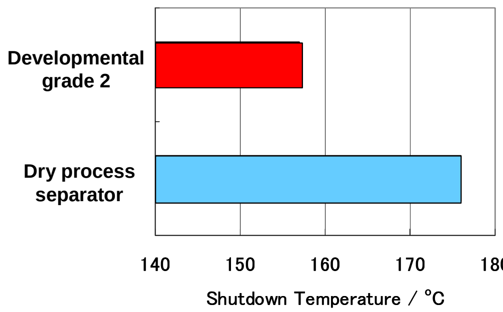

Figure 3. Shutdown temperatures measured by Impedance changes of model cells at elevating temperature

Shutdown performance was also evaluated using model cell to simulate it in the battery. Impedance tests of model cells measured at elevating temperature were showed in figure 3. Cell temperature for impedance test was elevated from room temperature to around 200 ^{o}C at a ramp rate of 35 ^{o}C per minutes. Shutdown temperature was determined when impedance of cell reaches a point where cell function is nearly stopped. Two samples, a commercial dry process separator and a shutdown performance enhanced co-extruded one (developmental grade 2) were evaluated. Shutdown temperature of the cell using developmental grade 2 had lower shutdown temperatures than that for cells assembled with dry process separator. Shutdown enhancement was confirmed not only by separator itself but also by model cell using separators.

Figure 4 showed a spider chart comparing our standard commercial mono layer grade (E25MMS) and co-extrusion developing grade (developmental grade 2) having low shutdown function. E25MMS is well-known for its excellent shutdown performance. Developmental grade 2 has better thermal safety while retaining other separator's properties at the same level to E25MMS. The combination of tailored polyolefin with co-extruded wet process design enables us to enhance the separator's shutdown performance.

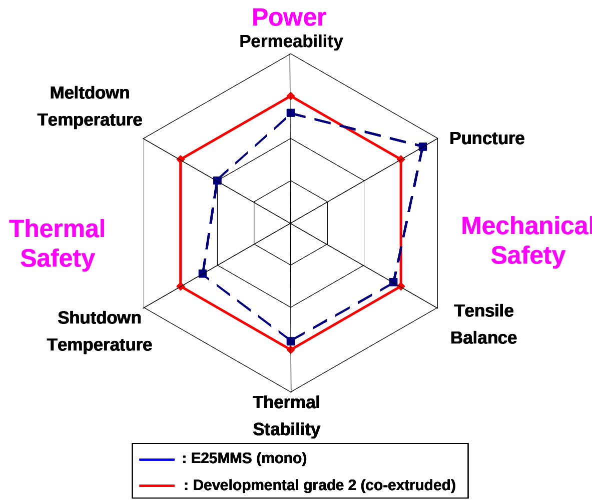

Figure 4. Spider chart for comparison of a prototype having wider safety margin and standard mono layer grade (E25MMS)

3 Concluding Remarks

A new technology was developed to broaden safety margin of batteries as an extension of our Co-extrusion Separator Technology Platform. The co-extrusion technology provided the improvement of melt integrity which was confirmed by TMA strain behavior, visual observation, AFM observations and impedance result.

Tonen's fundamental knowledge of separator technology allows continued improvement in separators with low strain which results in good heat shrinkage.

ExxonMobil's capabilities in polyolefin science enabled us to control separator's shutdown performance. The combination of co-extrusion technology and specially tailored polyolefins should bring us wider safety margin by low shutdown temperature and high melt integrity.

The new generation separators were produced using Tonen's proprietary wet fabrication process and co-extrusion of ExxonMobil's specially tailored polyolefins. New developing grades expanded co-extrusion technology platform. This broadened separator portfolio allowed HEV/EV lithium ion battery to be lighter and more durable, contributing to system cost reduction, safety, and improvements in design flexibility.

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