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Thermomechanical analysis and durability of commercial micro-porous polymer Li-ion battery separators

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ABSTRACT

Static and dynamic thermomechanical analysis was performed with a dynamic mechanical analyzer (DMA) to identify thermal and mechanical transitions for commercially available polymer separators under mechanical loading. Clear transitions in deformation mode were observed at elevated temperatures. These transitions identified the onset of separator "shutdown" which occurred at temperatures below the polymer melting point. Mechanical loading direction was critical to the overall integrity of the separator. Anisotropic separators (Celgard 2320, 2400 and 2500) were mechanically limited when pulled in tensile in the transverse direction. The anisotropy of these separators is a result of the dry technique used to manufacture the micro-porous membranes. Separators prepared using the wet technique (Entek Gold LP) behaved more uniformly, or biaxially, where all mechanical properties were nearly identical within the separator plane. The information provided by the DMA can also be useful for predicting the long-term durability of polymer separators in lithium-ion batteries exposed to electrolyte (solvent and salt), thermal fluctuations and electrochemical cycling. Small losses in mechanical integrity were observed for separators exposed to the various immersion environments over the 4-week immersion time.

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1. Introduction

Separator membranes are critical components of lithium-ion battery cells. Battery separators are micro-porous polymer membranes that electronically isolate the positive and negative electrodes, are easily wetted by an ion conducting liquid electrolyte and must be mechanically robust. While separators are electrochemically inactive components of a Li-ion cell, chemical degradation or mechanical failure of the separator in lithium ion battery cells can result in internal shorting and initiate thermal runaway [1,2]. The thermal stability of polymer separators is generally reported as the softening and melting temperatures. There is a need to characterize both the mechanical and thermal performance of polymer separators to understand how the membranes respond to elevated temperature under a constant or mechanical loading. Separators must be strong enough to withstand the cell winding process [3] and robust mechanical properties are necessary even above the shutdown temperature [4]. The purpose of this paper is to show the application of thermomechanical techniques to better characterize transition temperatures in polymer separators under static and dynamic loads as well as to observe mechanical durability due to environmental exposures: low temperature heating, electrolyte soaking, and electrochemical cycling.

The manufacturing process used to fabricate polymer separators dictates the orientation, size and shape of the pore structure as well as the crystallinity and mechanical behavior of the membrane. Two processing techniques are commonly used to produce micro-porous polymer separators for liquid nonaqueous lithium ion batteries. "Dry" processing of thermoplastic olefins utilizes extrusion to bring the polymer above its melting point and form it into the desired shape. Subsequent annealing and stretching processes may also be done to increase the crystallinity and orientation and dimension of the micropores [3,5]. Slit-like micropores or voids are formed by cold-drawing which causes stacked lamella to separate in the machine direction [6–8]. Upon cooling, crystallization of transverse tie-chains provide support for the porous structure. Orientation is dictated by annealing and extrusion at high speed and using high molecular weight polymers such as polyethylene and isotactic polypropylene [5,6]. The result is thicker and more pronounced lamella aligned along the extrusion direction after annealing [6] causing them to be anisotropic [9], meaning the mechanical properties along the extrusion direction (longitudinal) are superior to the lateral (transverse) direction [3]. "Wet" processing of polyolefin separators is done with the aid of a hydrocarbon liquid or low molecular weight oil mixed with the polymer resin in the melt phase [10]. The melt mixture is extruded through a die similar to the dry processed separators. Once in a sheet orienta-

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Table 1
Technical data for commercially available polymer separators used in Li-ion battery cells.

Property	Commercial polymer separators[a]			
	Celgard® 2320	Celgard® 2400	Celgard® 2500	Entek® Gold LP
Material	PP/PE/PP	PP	PP	UHMWPE
Thickness, μm	20	25	25	19.4
Porosity, %	41	41	55	37
Pore size, μm	$d = 0.027$	$d = 0.043$	0.21×0.05	–
Gurley, s 100 cm^{-3} (JIS)	530	620	200	394
Puncture strength, g	360	450	>335	432

[a] Data taken from technical information brochures or certificate of analysis [12,21–23].

tion, the oil is extracted leaving behind a solid polymer membrane with random network of micro-voids. Since the structure of a wet-process separator is not induced mechanically, both pore structure and mechanical strength are not directionally dependent or oriented [10,11] and the separators are nearly isotropic within the film plane. A complete and comprehensive review of battery separators and manufacturing processes can be found in Refs. [3,10,11].

Four micro-porous polymer separators were obtained from two industry leading manufacturers. Table 1 provides the manufacturer specifications for the separators studied. Separators can exist as individual polymer films or multi-layered laminates. Celgard 2320 is a 3-layered laminate with a polyethylene (PE) core between two polypropylene (PP) skin layers. All other separators tested here are single-ply films. Celgard 2400 and 2500 are composed of single-layer isotactic polypropylene manufactured via thermal "dry" processing into axially oriented sheets. Scanning electron characterization by Sarada showed Celgard 2500 ellipsoidal pore dimensions to be 0.4 μm long and range from 0.2 to 0.15 μm wide [8] although these dimensions differ from the more recent technical data provided by the manufacturer [12]. Entek Teklon Gold LP separators are manufactured via the "wet" casting technique in which ultra-high molecular weight polyethylene (UHMWPE) is co-extruded with a plasticizer which is removed in post-processing [13] to yield a biaxially oriented cross-stitch pattern. The ASTM Gurley number is a membrane permeability indicator and is approximately proportional to the square of the tortuosity ($\sim\tau^2$) [14]. The lowest Gurley number is for 2500 which is expected due to its high porosity and large pore dimensions.

2. Experimental

X-ray diffraction (XRD) was done with a Bruker D8 Advance X-ray powder diffractomer to observe bulk crystallinity changes within the separators before and after environmental exposure. Crystallinity changes as a result of thermal rearrangement and molecular movement is best characterized with thermal analysis. Thermal properties such as melt temperature and melting endotherm were determined from simultaneous thermal analysis (STA). Polymer separator samples (10–15 mg) were loaded into uncovered alumina crucibles and heated from 35 °C to 700 °C at a heating rate of 10 °C min^{-1} under flowing argon. The degree of crystallinity was calculated according to Eq. (1) [15]:

$$X_c = \frac{\Delta H_m}{\Delta H_m^\circ} \times 100\% \quad (1)$$

where ΔH_m° is the melting enthalpy of a polymer single crystal with for polypropylene and $\Delta H_{m,PE}^\circ = 281.1\ J\ g^{-1}$ for polyethylene. The degree of crystallinity for the individual PE and PP crystalline components of the multi-layered Celgard 2320 should be considered an estimation with several assumptions. The estimation assumes uniform pore volume and thickness of the constituent layers and should not be considered a standard for the structural morphology of the separator.

Thermomechanical measurements were recorded with a TA Instruments 2980 DMA in tension to observe transitions in the bulk properties. Dimensional changes (shrink and elongation) were recorded under a static load of 0.015 N (1.8 g) for rectangular specimens (18 mm length × 9 mm width) while the temperature was increased 10 °C min^{-1} from 35 °C until the separator fractured or surpassed the travel distance of the DMA moving clamp (~40 mm). The percentage strain was calculated by Eq. (2) where $\%\varepsilon > 0$ implies a positive strain or film "extension" and $\%\varepsilon < 0$ implies a negative strain or film "shrinking." Three samples were tested under each condition.

$$\%\varepsilon = \frac{l - l_o}{l_o} \times 100\% \quad (2)$$

The application of a dynamic oscillatory force on the mechanical properties of polymer separators at elevated temperature was measured through DMA. A dynamic load of 0.015 N was applied at a frequency of 1 Hz to rectangular specimens (18 mm length × 9 mm width) in tension between 40 and 120 °C to analyze the material response (displacement, storage modulus, loss modulus and tan δ) to an oscillatory tensile force. The thickness of the specimens varied as shown in Table 1. The storage modulus, E', is the measure of the elastic energy stored within a material under deformation can be elucidated with this technique. The advantage of DMA is that we can obtain a modulus value each time a sinusoidal tensile force is applied across a temperature range [16]. This can be used to predict long-term performance at elevated temperatures and under applied mechanical loads. The above characterization technique was performed on "as-received" polymer separator materials as well as separators exposed to three separate conditioning environments: (1) 55 °C anneal in air for 4 weeks, (2) submersion in a 1 M $LiPF_6$ electrolyte in ethylene carbonate/propylene carbonate/dimethyl carbonate (1:1:2) solvents for 4 weeks, and (3) cycled in $LiCoO_2$/MCMB pouch cells between 3.0–4.1 V for 100 cycles.

3. Results and discussion

3.1. Physical characterization

3.1.1. Morphology

XRD patterns show a high degree of crystallinity and orientation, a result of the manufacturing process to fabricate these materials (Fig. 1). Celgard 2400 and 2500 have sharp and distinct peaks around $2\theta = 14.0°$, 17.0°, 18.5° which is characteristic of isotactic polypropylene [17]. The Entek Gold LP sample, Fig. 1(d), displays diffraction peaks at approximately 21.5° and 23.9° typical of semi-crystalline polyethylene with a high molecular weight [18]. The diffraction pattern for Celgard 2320, Fig. 1(a), displays both sets of peaks for polyethylene and polypropylene due to its multi-layered laminate design (PP/PE/PP). The XRD penetration depth is sufficient enough to resolve the under layer in a multi-layered separator. The effect of immersion environment: 55 °C anneal, and post electro-