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Test Method

Thermal expansion/shrinkage measurement of battery separators using a dynamic mechanical analyzer

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ABSTRACT

Polymer separators for lithium ion batteries are thin, porous membranes of 20–30 μm thickness. At elevated temperatures, some separators can shrink considerably. To predict the deformation and stresses in the separator in battery cells, it is necessary to measure the expansion/shrinkage property of a separator as expressed by the coefficient of thermal expansion (CTE). The reported CTE measurement techniques for thin films have their limitations. This paper examines the use of a dynamic mechanical analyzer (DMA) for the measurement of the thermal expansion/shrinkage property of polymer separators. The effect of the dimensional change of the testing fixture was considered. The influences of the preloading levels and heating rates were investigated. The measurements were carried out for three common types of polymer based separator. The CTE as a function of temperature was determined from the DMA data. DMA offers continuous measurements in an automatic fashion, which is an efficient and convenient method to characterize the thermal expansion/shrinkage behavior of thin polymer films.

1. Introduction

In lithium ion batteries (LIBs), the separator provides electrical insulation between opposite electrodes while allowing ionic conductivity. The commonly used LIB separators are polymer based, thin, porous membranes of 20–30 μm thickness [1].

It is known that, with increasing temperatures, polymer separators first expand and then start to shrink before final fracture. The amount of shrinkage can be significant for some separators [1]. In a constrained condition, a larger shrinkage will induce higher stresses in the separator which may cause earlier failure. As the mechanical integrity of the separator is critical to the safety of LIBs, it is desired to predict the stresses and strains in the separator under extreme conditions such as thermal runaway. In such predictions, the coefficient of thermal expansion (CTE) is one of the required inputs. Because of that, it is critical to have a technique that can measure the thermal expansion/shrinkage of these films continuously and accurately.

The standard methods determine the CTE of a material through measuring the volume or lengthwise change of a free standing sample [2,3]. These techniques are not suitable for materials in the form of thin films.

For thin films, several CTE measurement techniques have been reported. A common method is laying an unconstrained sample on a flat surface in an oven with an optical window and using non-contact optical methods such as interferometry [4] or digital image correlation [5] to measure the dimensional change. For metal foils, the CTE can be measured using a bi-layer configuration with a substrate of known CTE [6]. The optical measurement requires special equipment. The bi-layer configuration is not suitable for polymer thin films because the stiffness of these materials are too low to generate needed deformation with commonly used substrates.

The thin film CTE measurement has also been attempted for a clamped sample. El-Tonsy [7] presented a system that measures the length change of a clamped polymer film sample under a small hanging weight. This system has some similarity to the thermal mechanical analyzer (TMA) and dynamic mechanical analyzer (DMA) commonly used in polymer characterization. TMA [1,8] and DMA [9–12] have been used widely in the characterization of battery separators. Baldwin et al. [9] characterized the shrinkage of battery separators under isothermal conditions using a DMA under tensile mode [9]. These works indicate the potential of TMA and DMA in thin film CTE measurement. The current study explores this possibility.

This paper presents a systematical investigation on the use of a DMA under tensile mode for the thermal expansion/shrinkage measurement of battery separators. Factors such as the calibration procedure, the influence of the tensile load and the temperature ramp rate were

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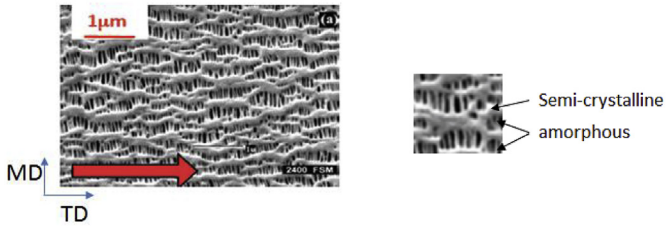

Fig. 1. Surface microstructure of Celgard® 2400 [1]. The two in-plane material directions are referred to as the machine direction (MD) and the transverse direction (TD).

examined. Using the established method, the measurements were carried out for three common types of LIB separator from ambient to the maximum temperature that the measurement can be performed.

2. Experimental

2.1. Materials

Three representative separators were investigated in this work. They were: (1) Celgard® 2400, a monolayer PP; (2) Celgard® 2325, a trilayer PP/PE/PP; and (3) Celgard® Q20S1HX, a ceramic coated trilayer PP/PE/PP. The film thickness was 25 μm for 2400 and 2325, and 20 μm for Q20S1HX.

Fig. 1 shows the surface microstructure of a typical PP separator [1]. As seen, the pores are a fraction of micrometer long and tens to hundred nanometer wide, with splits. The fibrous like structures that separate the splits are amorphous. The thick regions are semi-crystalline. This unique microstructure is formed through a multi-step process including melt-extrusion, annealing, stretching and heat fixation [1]. The resulting material is highly anisotropic. The separator is usually treated as an orthotropic material with the two in-plane material directions referred to as the machine direction (MD) and the transverse direction (TD).

2.2. Measurement

The experiment was performed with a TA Q800 DMA under tensile mode. DMA is a common mechanical testing equipment to characterize the viscoelastic behavior of materials. Fig. 2 shows the experimental set-up. The sample was gripped at both ends with tension clamps. Then, the cell was closed and the temperature ramped. During the test, a constant force was maintained and the lengthwise variation of the sample gage length was measured.

The samples, in the form of long strips with a length of 45 mm and width of 6 mm, were cut using a razor blade. The sample width was then measured, on a flat surface, using a caliper. Samples were prepared both along MD and TD, as shown in Fig. 3. In DMA measurement, the testing length of the samples was about 15 mm.

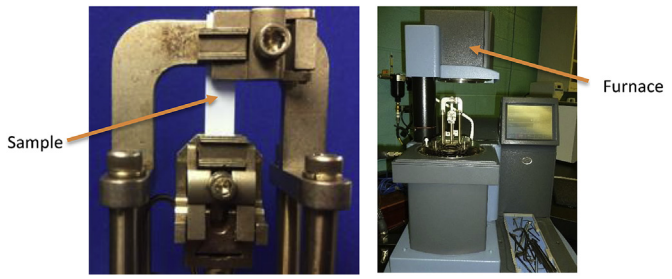

Fig. 2. (A) A sample is mounted in the tensile clamp in DMA Q800. (b) The furnace will then be closed for temperature ramp.

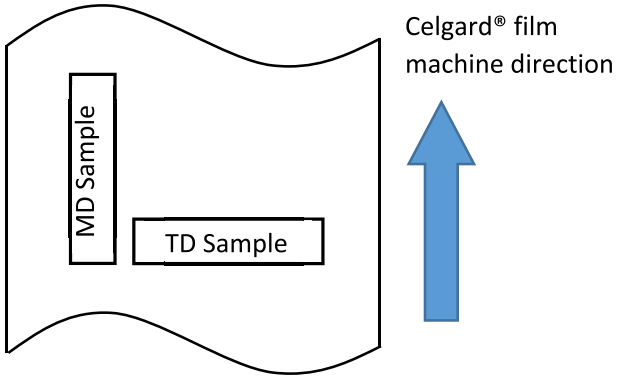

Fig. 3. The MD sample and TD sample.

Celgard® 2400 was tested first to investigate the effect of the test parameters such as the level of the tensile load and the temperature ramp rate. The experiments were performed at multiple heating rates and force levels. A preload of 0.01 N and 0.001 N was selected for the MD and TD samples, respectively, and a heating rate of 3 °C/min was selected for both samples. The results of these investigations will be presented in Section 3.1.

2.3. Calibration

Prior to the CTE measurement, the DMA needs to be calibrated using a material with known CTE. In this work, the calibration was performed with Al thin foil of 25 μm thickness with a purtiy of 99%. The sample dimensions and their mounting in the DMA were the same as that described in 2.2. The measurement was performed under a small tensile loading of 0.01 N over the temperature range from ambient to 220 °C with a heating rate of 3 °C/min.

Fig. 4a presents the measured grip displacement with increasing temperature obtained with the Al samples. The slopes of the curves appear to be negative, implying a negative CTE, i.e. shrinkage instead of expansion. For a sample with a known CTE, the change in sample gage length with temperature can be calculated. For pure Al, the CTE is reported as 24.5×10^{-6}/°C over the range of 20–200 °C [13]. The displacement predicted this way is presented by the dashed line in Fig. 4a. The discrepency between the predicted curve and the measuremed curves indicates that the measured grip displacement included the contribution from other components in addition to that of the sample.

In TA DMA systems, the grip displacement is measured by a sensor located on the drive shaft [14]. The measured displacement includes the dimensional change of the sample, the grip, and the drive shaft relative to a stationary component [14], in addition to that of the sample. The standard calibration procedure for the DMA uses a steel sample and the calibration is performed at ambient temperature. Based on the calibration, the contribution of the testing fixture compliance is automatically excluded from the DMA output. This is sufficientlly accurate for mechanical testing, as verified by comparing the DMA data with the digital image correlation measurement [15]. In measurements over a temperature range, all components, including the stationary component, will experience thermal expansion/shrinkage. In mechanical testing, the strain due to the dimensional change of the testing fixture is usally negligible compared to the deformation experienced by the sample. For CTE measuremnts, additional calibration is needed. The calibration should be performed with the same experimental set-up and under the same testing condition.

To determine the true dimensional change of the sample, the contribution of the testing fixture must be known in advance. This amount is designated as $\Delta l_{calibration}$, determined by the difference between the predicted dimensional change $\Delta l_{predicted}$ over the gage length l of the