Microfiber/Nanofiber Lithium Ion Battery Separators for Higher Power and Faster Recharge

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Abstract: *Thermal behavior of battery separators used in lithium ion batteries are compared. Dry-type polyolefin separators are compared to nanofiber based nonwoven separators. Behavior is similar below about 70 C, but above that temperature the polyolefin separators begin to shrink and then melt. Nonwoven separators that have not been dried show a water elution between 50 and 150 C. Separators also show very different behavior under exposure to flame while saturated with electrolyte, with the polyolefin separators catching fire and burning, eventually being reduced in size by >50%, while the nonwoven separators retain their shape and size, but do char in some areas. In summary, the nanofiber-based battery separators produced by Dreamweaver show dramatically higher thermal stability as well as greatly improved behavior when exposed to flame.*

Keywords: lithium ion; membrane; battery separator; nanofiber.

Introduction

There have been several instances of thermal events in lithium ion batteries that have recently achieved a high profile in the media. These events make improved safety to prevent and mitigate the damage from thermal events in lithium ion batteries of considerable importance. This study compares the thermal properties of commercial dry-processed separators for lithium ion batteries made from polypropylene and from a tri-layer of polypropylene and polyethylene to separators made from wet-laid combinations of nanofibers and microfibers.

Methods

Five commercial separators were obtained, including:

1. Dry Process PP, 25 micron, obtained from MTI.
2. Trilayer Dry Process PP/PE, 25 micron, obtained from MTI
3. Dreamweaver Gold, 25 micron
4. Dreamweaver Silver, 25 micron
5. Dreamweaver Silver AR, 30 micron

Each of these separators were tested at the Clemson Materials Science and Engineering Department for TMA, DSC, and TGA, with the following condtions.

TMA: Sample size 22 mm length x 10 mm width, tested in air with static force 0.001 N (1 gf), tested in both machine direction and cross direction from 25 – 300 C

DSC: Sample size ~4 mg tested under Helium gas, ramped from 0 to 300 C at 10 C/min, hold 0.5 min, then ramp 300 to 0 C at 10 C/min.

TGA: Sample size ~2.5 mg, tested under Nitrogen gas, ramped from 25 to 1000 C at 10 C/min.

For flame exposure, three separators were tested, the dry process PP, 25 micron, the Dreamweaver Silver and the Dreamweaver Gold. Roughly 3" squares were cut from each, and saturated in lithium ion electrolyte (mixture of EC, DEC and DMC at equal ratios with 1M LiPF6). These were then laid on a piece of aluminum foil with an excess of electrolyte, and the electrolyte was lit and allowed to burn until the flames self-extinguished.

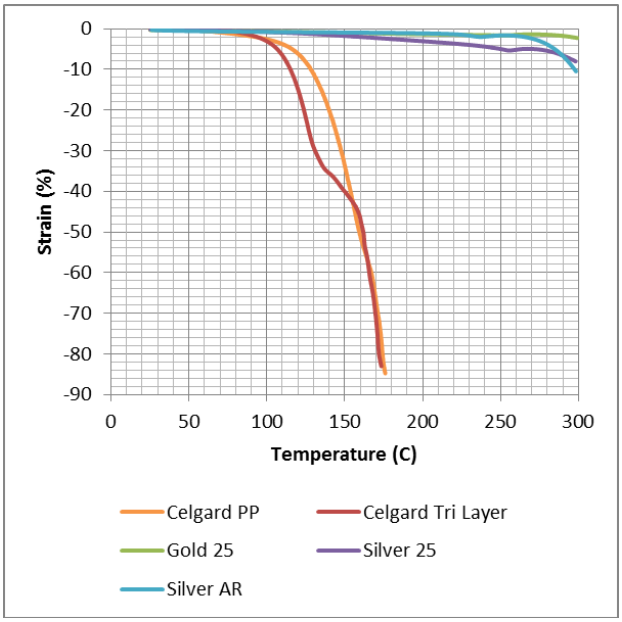

Figure 1: Machine direction TMA of five separators with expanded scale.

Results

TMA

The results are shown on the following pages. For TMA, there are dramatic differences in the behavior of the different separators above about 75 C, with the olefin materials shrinking sharply in the machine direction and undergoing catastrophic shrinkage above 100 C. The nonwoven materials shrink very little, less than 5%, up to 250 C, with the Dreamweaver Gold material showing only 2% shrinkage up to 300 C.

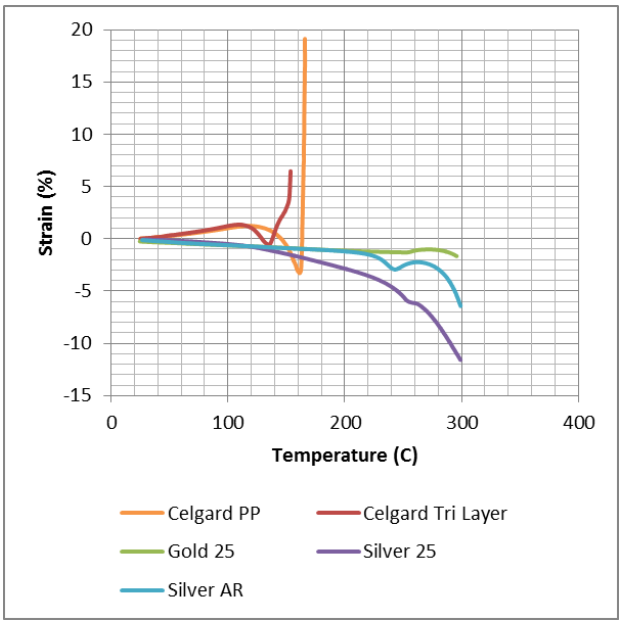

Figure 2: Cross direction TMA of five separators.

In the cross direction, the polyolefin separators have such low strength that when they begin to soften above 50 C, they stretch even with only 0.1 g/mm of force applied. At slightly higher temperatures, they begin to shrink, but then the softening causes the films to become too weak and they break under this tiny force. The Dreamweaver separators show almost isotropic shrinkage, with all values below 10% even up to 300 C, and the Dreamweaver Gold shrinking less than 2% up to 300 C in both directions.

DSC

The DSC runs show expected behavior. The dry-process PP separator shows only the melting peak centered near 165 C, while the tri-layer material shows two peaks, one near the polyethylene melt temperature of 130 C, and the other slightly lower than the normal PP melt temperature, centered around 158 C. The Dreamweaver separators show only a water elution peak centered around 100 C, and a melt peak for poly ethylene terephthalate, centered at 250 C. Note that the Dreamweaver separators were purposefully not dried so that the water evaporation could be discussed in a separate section, below.

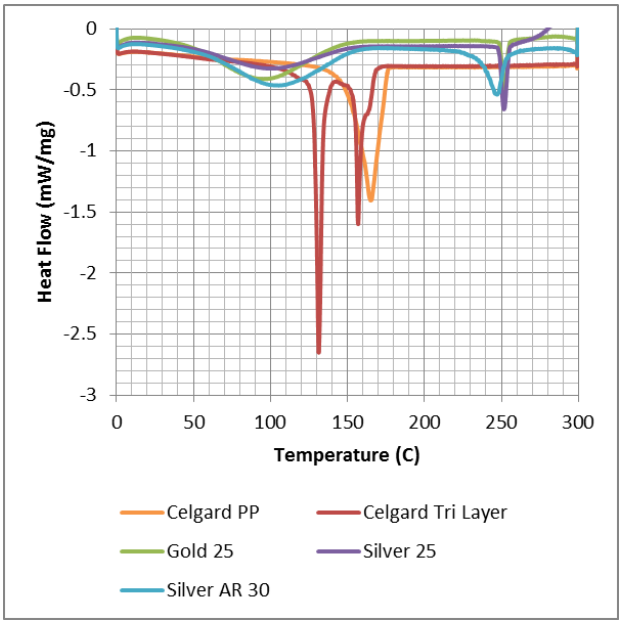

Figure 3: DSC of five separators.

TGA

All of the materials are stable under TGA up to 280 C. The olefin materials begin a sharp mass loss at 320 C, which goes to nearly 100% mass loss by 440 C, even in a nitrogen environment. In stark contrast, Dreamweaver Silver and Gold start to lose mass around 280 C, but then retain >25% mass even up to 500 C, and even higher for Silver. As is discussed below, this results in far different performance when exposed to a flame.

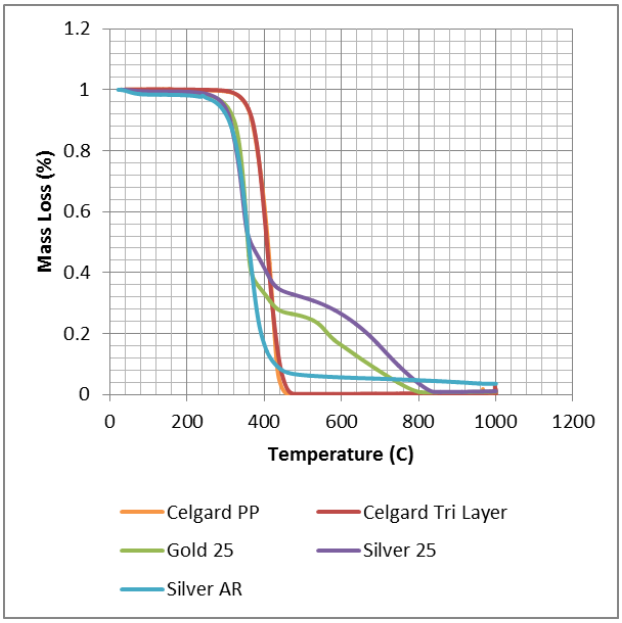

Figure 4: TGA of five separators.

Discussion

Water Evaporation

The polyolefin separators do not hold water, and so no evidence of water evaporation is present in any of the thermal studies. The Dreamweaver separators, all of which contain cellulose nanofibers, do show water evaporation with a peak that centers around 100 C, with all water having evaporated by 150 C when exposed to this thermal ramp of 10 C/min.

The three Dreamweaver materials, which were not prepared in any specific humidity environment but rather taken straight from the package, show water content that of 0.6% for Silver, 1.1% for Gold and 1.7% for Silver AR. Owing to the thermal stability of the materials, drying of the separator can be accomplished in reasonable time frames at temperatures ranging from 120 – 140 C, depending on the size of the roll that is to be dried.

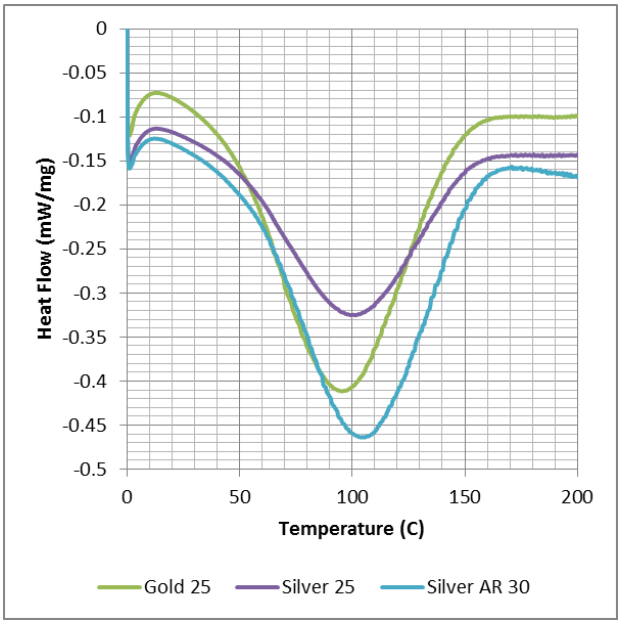

Figure 5: DSC of Dreamweaver separators highlighting the water evaporation peak.

Behavior on Exposure to Flame

Given the different thermal behavior shown and discussed above, and the fact that these separators perform their function while saturated in a mixture of flammable organic solvents, we thought a short study on how the separators may behave when exposed to flame would provide interesting results.

Three separators were tested—the polypropylene dry-process separator, Dreamweaver Silver and Dreamweaver Gold. All were saturated with lithium ion battery electrolyte and then placed on aluminum foil in an excess of electrolyte. The electrolyte was then lit, and all three separators were engulfed in flame as shown in the picture below.

After the flames self-extinguished, the Dreamweaver Silver and Dreamweaver Gold separators each retained their shape, showing some charring. The polypropylene dry-process separator began shrinking and melting immediately, and continued burning after the electrolyte had extinguished, finally being reduced to a few residual plastic balls and clumps. While this is not the same as a battery catching fire, the ability of a separator to retain its separation capability in the presence of burning electrolyte is likely to lead to better battery safety if the cell is engineered properly.

Figure 6: Photo of tri-layer, Dreamweaver Silver and Dreamweaver Gold separators that have been saturated in electrolyte and then lit on fire.

Figure 9: Photo of tri-layer, Dreamweaver Silver and Dreamweaver Gold separators after having been engulfed in flaming electrolyte.

Summary

In summary, five separators were tested for behavior at high temperature under TMA, DSC and TGA, and then also in a simulated flame test in the presence of lithium ion battery electrolyte. From these studies, the following conclusions can be drawn:

- Polypropylene and tri-layer separators shrink dramatically at temperatures above 100 C, and also soften at temperatures above 75 C.
- Dreamweaver nanofiber separators have <10% shrinkage up to 300 C, with Dreamweaver Gold having less than 2% shrinkage up to 300 C. The shrinkage behavior of Dreamweaver separators is roughly isotropic.

- Even under a tiny force of 0.1 g/mm, polypropylene and tri-layer separators extend toward a break in the cross direction at temperatures of 150 – 160 C.
- Mass loss in a Nitrogen atmosphere for polypropylene and tri-layer separators begins at 320 C and is nearly complete by 400 C.
- Mass loss in a nitrogen atmosphere for Dreamweaver separators begins around 280 C, but significant mass is retained up to over 600 C in the case of Dreamweaver Silver and Dreamweaver Gold.
- Dreamweaver separators need to be dried, and the water evaporates between 50 and 150 C when ramped at 10 C/min. Polypropylene and tri-layer separators show no evidence of water.
- When saturated with electrolyte and exposed to a flame, the polypropylene separator first shrinks catastrophically, then burns until long after the electrolyte has self-extinguished, finally stopping when the separator residue only covers a small portion of the original area.
- When saturated with electrolyte and exposed to a flame, Dreamweaver Silver and Dreamweaver Gold retain their shape while the electrolyte burns, and do show some charring but retain essentially the same shape and size as they did before the electrolyte was lit.

Acknowledgements

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References

1. Huang, X. (2011). Separator technologies for lithium-ion batteries. Solid State Electrochem, 649-662.
2. Jianjun Zhang, Q. K. (2013). A highly safe and inflame retarding aramid lithium ion battery separator by a papermaking process. Solid State Ionics, 49-55.
3. Lara Jabbour, R. B. (2013). Cellulose-based Li-ion batteries: a review. Cellulose, 1523-1545.