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A review of physical properties of separators for valve-regulated lead/acid batteries

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Abstract

The microglass separator has been used from the conception of valve-regulated lead/acid (VRLA) technology. There is increasing recognition that the separator has a critical role in battery performance. Research is supporting the position that compression exerted by the separator has an important role in premature capacity loss. Some companies have suggested that the separator compression set/creep plays a critical role in the battery failure mechanism in float applications. ALABC studies have shown that designs with higher compression improve the cycle life of batteries. Increasing numbers of manufacturers are designing their separators around the end-application of the battery. The separator in a VRLA battery is not an inactive spacer/barrier, as in a flooded lead/acid cell. Instead, these separators function as a key element, the third electrode. This paper reviews aspects of the microglass separator used in VRLA batteries. Information is provided to make a better separator selection, since a 100% microglass media, or any recombinant battery separator mat (RBSM) for a VRLA battery has a critical role in assuring the performance of the battery. A poor design can thus decrease the expected life of the battery.

Keywords: Valve-regulated lead/acid batteries; Microglass separators; Compression; Lead/acid batteries

1. Background

A microglass separator was the first separator to be used in a valve-regulated lead/acid (VRLA) batteries. This continues to be the separator of choice in most VRLA batteries. The microglass separator is a wet laid non-woven paper and is manufactured on a paper machine. The type of paper machine used by the manufacturer can influence the separator properties. Three properties — porosity, uniformity, fibre directionality — are important attributes that can be influenced by the type of former used. The separator has gone through many changes and today's separators offer the battery manufacturer a significantly more consistent and reliable product.

A microglass non-woven paper was originally selected because the microglass separator has a very fine fibre structure and can often absorb its own weight of acid. The fine fibre structure of the microglass allows the separator to have a very high porosity. The glass fibre, which has a zero-contact angle with the acid, is durable in the acid environment, and the fine fibre structure also has good resiliency to allow for a sustained pressure against the plate. The microglass separator has a high porosity in the 90–95% range and is very conformable. The separator can adapt to imperfections in the plate surface. A hard, rigid material would have difficulty conforming to the plate and, therefore, would not wet the total plate. A further important attribute of the microglass is the fact that the fibre is inorganic and, thus, has extremely high temperature stability. The microglass fibre structure will not melt in a thermal runaway situation. This can happen with an organic separator manufactured with low-temperature polymers.

In the infancy of the VRLA battery, the glass-fibre chemistry that was used differed greatly from the chemistry employed today. Initially, less acid-resistant fibres were used and they had higher leachable heavy metals such as zinc. Today, separators are supplied with tighter tolerances for properties such as thickness and grammage. Specifications were much wider in the past. Early separator thickness specifications may have been as wide as 20%. With today's tighter specifications and better understanding of the importance of the compression inside the cell, present-day VRLA batteries should provide greater reliability.

The separator being supplied today has improved quality, uniformity and value in comparison with the separator of the early and mid 1980s. As more is being learned about the role of the VRLA separator, the physical characteristics of the microglass separator, and how these characteristics impact on a battery, improved performance is being obtained by the industry. Compression is one property that is being proved to be a critical characteristic. Compression is being linked to

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premature capacity loss (PCL) [1]. Due to the importance of compression, this paper focuses on this physical attribute.

2. Discussion on compression

Compression is one of the key physical attributes of a VRLA separator. Increasing the compression exerted by the separator is one of the prime factors to longer battery life. In designing a battery, the engineer will use a certain compression factor to construct the cell. The compression factor is based on a reported value of thickness based on some measurement protocol. Thus, the thickness measurement is another key-design attribute of a VRLA battery. One problem is that, over the years, many protocols have been used to determine thickness. Some companies used different pressure foot and different loads. The Battery Council International (BCI), through a consensus process, selected the use of a thickness test that has a 29 mm anvil and a 10.34 kPa load. The Japanese Industrial Standards use a 20 kPa load with a 100 cm^2 sample size. In the past, thickness may have been determined with various anvils and different loadings, i.e. 4.8 kPa, 50 kPa, etc. Using this historical reference to determine performance based on separator design, and extrapolating it for today's tighter standards, may be difficult.

In the measurement of thickness, changing the size of the pressure foot does make a difference. Using a 29 mm diameter pressure foot, at 20 kPa, versus 100 cm^2 contact area at the same loading, can result in a 20% difference in reported thickness. This can also be seen if this test is done at 10 kPa, but the difference observed is much smaller, namely, in the 3–5% range. Many companies have used a design of 20–25% compression based on the reported thickness at 10 kPa. If differences exist between thickness measurements made with different size platens, then what is the compression? The thickness obtained with the 100 cm^2 platen seems more representative of actual battery conditions. Increasing loads to measure thickness has another influence, which is to decrease the standard deviation of the measured values.

Compression can be determined by using the BCI test. This test measures the thickness of the separator under various loads. The thickness is obtained both under these loads and after the loads are removed. The latter is called compression recovery. Both values are then plotted. Figs. 1 and 2 are typical compression and recovery curves. The curves are for Hovosorb® II microglass separator at 240 and 300 g m^{-2}. These separators have a surface area of 1.0 m^2 g^{-1}. The graphs show the compression curve for a separator that was dried and then re-wetted with sulfuric acid. The amount of sulfuric acid added was chosen to represent a typical saturation level inside a battery. The graph shows that partial saturation decreases the thickness of the separator at a given load. This is evident by examining the recovery curve. This is one reason why when acid is added into the battery, a relaxation of the case can sometimes be observed. One area where a good standard test should be developed is for a longer-term compression test.

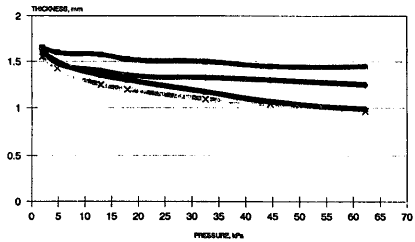

Fig. 1. Compression curve for Hovosorb II 240 GSM microglass separator.

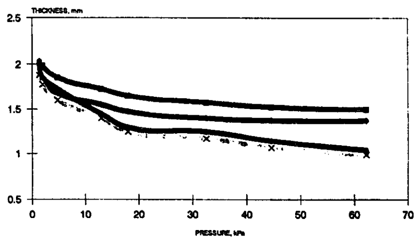

Fig. 2. Compression curve for Hovosorb II 300 GSM microglass separator.

The compression remaining inside the battery after the acid is added is another critical factor; if there is insufficient compression, the separator will not have contact with the plate. This lack of plate-to-separator contact may develop during battery service as the battery dries out. This is especially true if the design compression did not account for the saturated recovery curve of the glass separator at the lower saturation levels. A good reference to this effect has been presented by Culpin [2]. This discussed the relationship of a microglass separator's thickness to the degree of saturation in the separator. This physical attribute of the separator is of great importance since VRLA batteries will dry out. Dry-out occurs from plastic permeability, corrosion of the lead, and from the valves. The design release-pressure of the valves may be too low and allow the valve to open unnecessarily, thereby venting gases. The valve may open, and then stick in an open position. Valves sticking open will cause the negative electrode to sulfate by reaction with the oxygen from the outside air.

A high compression inside the battery is sometimes a compromise with other factors such as having to force the stack into the jar. One way to get a measurement of the dry compression force is to use a force gauge to insert the stack into the jar and to record the value. In this way, a chart can be developed to control this important property.

3. Retention of thickness during saturation

To better understand the thickness retention property of a microglass separator after it has been compressed and then re-wetted, an experiment using a standard wicking column test was done. The separator was placed between sheets of plastic using a shim to provide the desired compression. The strip of separator was then allowed to wick up water. In addition to measuring the fluid that was imbibed, the thickness was also determined. Fig. 3 shows the results of this test on Hovosorb II, BG24017, manufactured on Hollingsworth and Vose's new No. 8 machine in New York.

The results represent a single experimental data point. A Plexiglass wicking tower was used to compress a separator 55% from its BCI thickness. Water was allowed to wick up the separator from a reservoir. After 24 h at the 55% compression, the apparatus was torn down and the fixture was taken apart. A sample was cut from the strip every 5 cm. The wet thickness was measured and the wet weight obtained. Samples were then dried, re-weighed, and re-measured for thickness.

The data indicate that at higher saturation levels, the separator has a greater change from the original thickness. The largest difference observed in this test was a 10% change. Fig. 4 is a trend chart that compares the amount separator saturation with the thickness lost at that level of saturation. The trend chart shows that as more fluid is absorbed, the greater is the dried thickness lost. In selecting the compression to use to build a battery, this variable must be considered. It should be noted that this experiment used a very high compression of 55%. It should also be remembered that as plates are discharged and charged, the plates will expand and contract. This causes the separator to experience compression and then relaxation.

Experiments using lower compression factors produced proportionally smaller, thickness losses. Figs. 5–8 show the results from additional studies using 40 and 20% compression on a standard 1.1 $m^2 g^{-1}$ surface area separator at 420 $g m^{-2}$. During the study, the surface tension of the water was measured. During the 24 h test period, the surface tension in the water reservoir changed from an initial value of 73 to 68.8 dyne cm^{-1}, while the fluid squeezed from the separator had a surface tension of only 51 dyne cm^{-1}.

4. Influence of draft of the battery case

Another influence on the separator compression inside the jar is the draft of the jar wall. The draft can result in a 10% change in compression from the top to the bottom of the plate. If a target compression of 25% is based on the opening in the middle of the cell, then there is a range of compression from

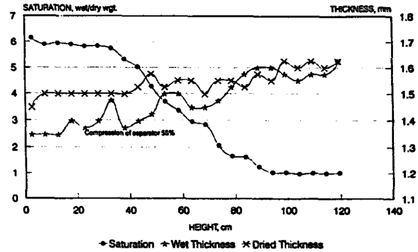

Fig. 3. Wicking vs. retained thickness.

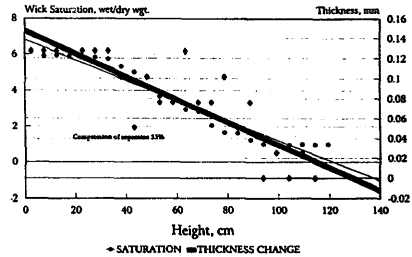

Fig. 4. Wicking vs. thickness trend chart.

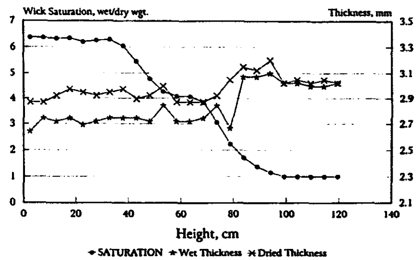

Fig. 5. Wicking vs. thickness, 20% compression.

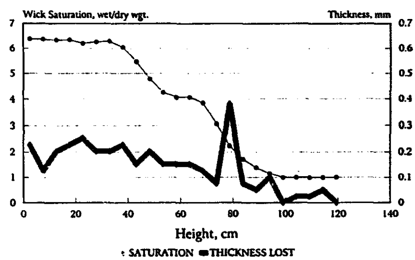

Fig. 6. Wicking vs. thickness lost, 20% compression.

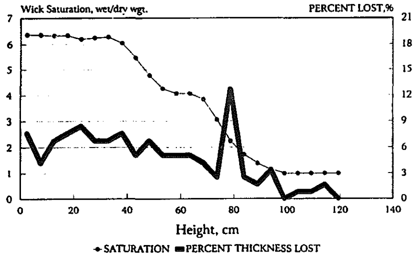

Fig. 7. Wicking vs. percent thickness lost, 20% compression.

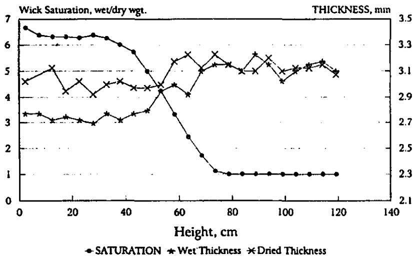

Fig. 8. Wicking vs. thickness lost, 40% compression.

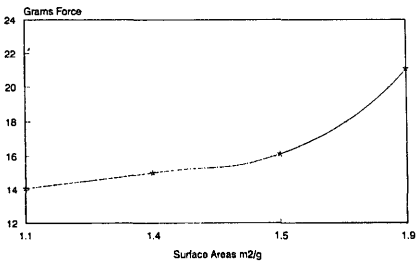

Fig. 9. Force to crush Hovosorb microglass separator.

20–30%. Most would agree that a design change from 20 to 30% is significant. This also has an influence on the separator's properties. Since the separator has uniform grammage from the top to the bottom of the plate, the separator would then have a much smaller pore structure at the bottom of the plate. This will cause slower acid-drip speed as the acid approaches the bottom of the plate. In addition, since smaller pores have greater forces to attract liquid, this could increase stratification.

5. Crush force of separator

An important design criteria of the microglass separator is the surface area. The separator's surface area influences the compression characteristics of the separator itself. A higher surface area improves the resiliency of the separator, increases the tensile properties, results in smaller pore structure, and increases the ability of the separator to be 'crushed'. Crushed separator is defined as a separator which has lost its ability to rebound under a given load. To get a determination of the force required to 'crush' the separator, different surface area materials were run through a pair of 76 mm diameter, rubber-covered rolls. Various loads were used while running a dry separator through this nip. Both dry and acid-saturated compression curves were performed on these samples. The 'crushing' is observed when the separator is acid saturated. Under dry conditions, this 'crushing' of the separator is not seen.

Although the above test gives only a rough estimate of the force required (see Fig. 9), it is clear that a relationship exists between surface area and the force required to 'crush' the material.

6. Uniform stack compression

In compressing a stack in a cell, do all separators compress equally? Studies done in the laboratory suggest that differences exist within a stack. If this is the case, then the manner in which the stack is compressed and assembled is important. The plastic used to make the case is also critical as is the ability of the plastic to hold the stack compression. What is the thermal creep stability of the plastic under high-temperature conditions? Will the plastic stretch and, thereby, decrease the compression inside the case?

7. Summary

1. The separators being supplied today are of improved design. They are supplied with tighter tolerances than in the past, and thus should produce more consistency in the batteries.
2. Compression inside the battery is an important design consideration. The design of the battery must take into account other factors that will affect the compression of the cell. Some of these issues are cell saturation, the type of glass used, jar drafts, the wall thickness and the history of how the battery was assembled.

3. Battery designs should move to higher compression inside the battery for improved performance. Compressions over 30% should be considered.
4. Greater understanding of the various components, especially the separator, is still needed to help this technology mature and to provide for improved reliability.

References

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[2] B. Culpin, *J. Power Sources*, *53* (1995) 127–135.