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Use of synthetic fibre reinforcement for improving the performance of AGM separators for VRLA batteries

N. Clement*
Bernard DUMAS, P.O. Box 3, Creysse 24100, France
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Abstract

Absorbent material made of 100% microglass fibre is well-known as a separator for valve-regulated lead-acid (VRLA) batteries and has been in use for about 20 years. As the VRLA battery market and demands on battery performance continue to grow, the electrical characteristics, productivity and reliability of VRLA batteries are being enhanced. Both the reliability and the electrical performance of the battery are linked to the AGM glass material. The properties of the AGM material impact the assembly route, defect rates, productivity, product cycleability, life, reliability, and recharge performance.

An AGM product range which contains synthetic fibres up to 30% in mass (the remaining 70% is still glass) has been developed. The reinforcement of the material with a specific organic fibre is showing very positive effects, both on intrinsic separator characteristics and, as a consequence, on the manufacturing, electrical properties and cycle-life of batteries. The AGM product has been used in the battery market now for more than 20 years. Based on this experience, new testing methods such as the fatigue test and internal pressure measurement have been developed. It is clear from such measurements that reinforcement with synthetic fibre has a positive impact on battery characteristics.

Keywords: Absorptive glass mats; Cycle-life; Reinforcement; Synthetic fibre; Valve-regulated lead-acid batteries

1. Introduction

Standard valve-regulated lead-acid (VRLA) batteries have been manufactured for many years with 100% microglass fibre separators, also called AGM (absorptive glass mat). Glass fibres are resistant to sulphuric acid at battery operating temperatures and exhibit excellent acid wetting (near zero contact angle). The strength of 100% microglass fibre AGM is provided by the physical interlacing of the fibres, which is achieved by the wet paper machine process. The fibres act as small springs when pressed between battery plates and can move and reorganize when acid is added to the mat.

The author's company has developed a specific range of separators which contain synthetic fibres in order both to improve mechanical strength and to restrict the porosity of the material. The synthetic fibres have shown very good behaviour in contact with acid and very good mechanical resistance to structural degradation. The synthetic fibre has a heterogeneous structure in which the inner fibre core provides strength and stiffness and the outer sheath assists binding by melting on the glass fibres during a specific step on the paper machine.

This paper describes the improvements and advantages given by synthetic fibre reinforcement.

2. Synthetic fibre structure

Absorbent glass material is made on a paper machine. Fibres are dispersed in water and then the process consists of removing water from the paper sheet that is formed on the paper machine head. The glass fibres are mainly bound together by mechanical interlacing. In the wet condition (acid or water), the liquid penetrates between the fibres. When an external force is applied, the fibres slip on to each other much more easily than when the AGM is dry. The synthetic fibres used in this development are heterogeneous, as shown in Fig. 1.

The fibre core is a strong polymer that does not change in shape or structure in acid and hot conditions. The outer part of the fibre is a polymer that can melt in the paper during processing. This melting makes synthetic fibres bind on to any glass fibre that touches them, as shown in Fig. 2. When the material returns to room temperature, the melted

* Tel.: +33-55-323-2105; fax: +33-55-323-3713.
E-mail address: ni-clement@bernard-dumas.fr (N. Clement).

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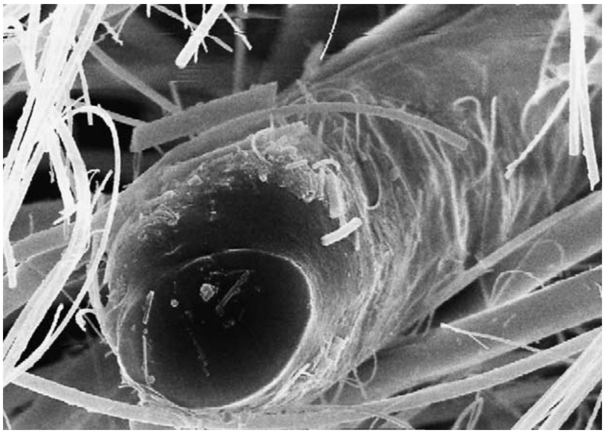

Fig. 1. SEM microscopic picture of synthetic fibres.

part becomes hard again and reinforces the glass mixture structure.

3. Mechanical properties

3.1. Puncture resistance dry and wet

Puncture resistance is the measurement of the force required to make a pin penetrate the separator, as described in Fig. 3 (Battery Council International—Test Method 214 to 3b-032). Puncture resistance is the highest strength measured while the pin penetrates the separator at 20 mm per min.

A series of measurements has been made on laboratory specimens in order to evaluate the specific impact of the synthetic fibre, with all the other parameters kept constant. As shown in Fig. 4, the more synthetic fibre is added to the AGM separator, the higher is the puncture resistance. This test has also been made on wet samples (de-ionized water). Here again, the puncture strength is increasing simultaneously with the amount of synthetic fibre, but most interesting is the difference between the dry and the wet conditions. There is almost 20% less puncture strength under wet than under dry conditions when no synthetic fibres are present.

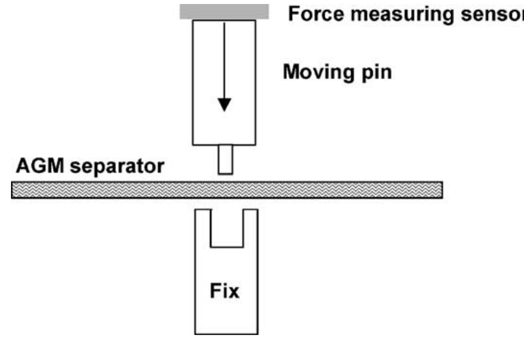

Fig. 3. Puncture resistance measurement.

This loss decreases to less than 5% when synthetic fibres are included. The effect can be understood by the fact that the binding points where synthetic fibres are melted on to glass fibres are not affected by the introduction of water, whereas the standard mechanical interlacing of glass fibres is weakened by the presence of water.

3.2. Tensile strength dry and wet

Tensile strength is the measurement of a strip of separator, 25.4 mm wide with a length of 100 mm, which is stressed to produce a strain rate of 10 mm per min. A series of measurements has been made on the same specimens as used for the puncture study.

As for puncture resistance, the more synthetic fibre is added to the AGM separator, the higher is the tensile strength (Fig. 5). This test has also been made on wet samples. Again the tensile strength increases with synthetic fibre amount and the difference between dry and wet tensile strength decreases proportionally with the amount of synthetic fibre.

3.3. Link between mechanical characteristics of AGM and battery processing

3.3.1. Battery assembly

During battery assembly, rolls of separators can be pulled along by an automated machine. In this phase, the sepa-

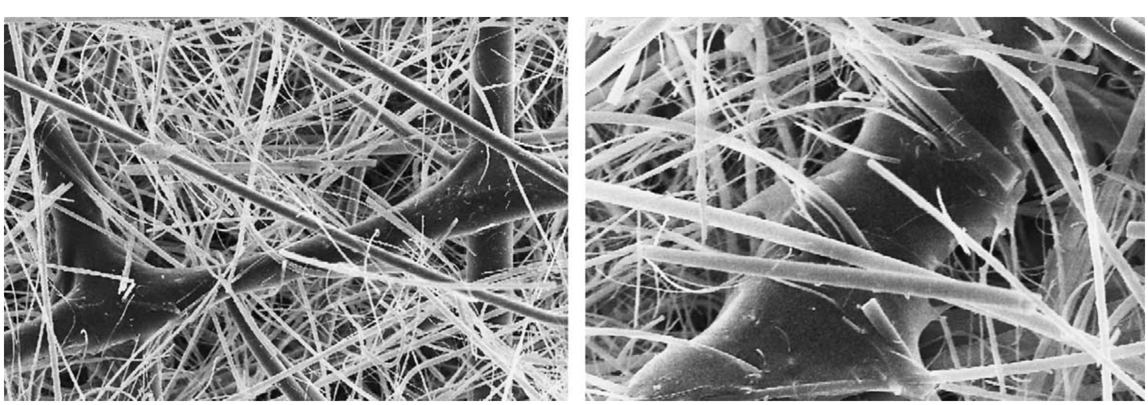

Fig. 2. SEM microscopic picture showing binding of fibres.

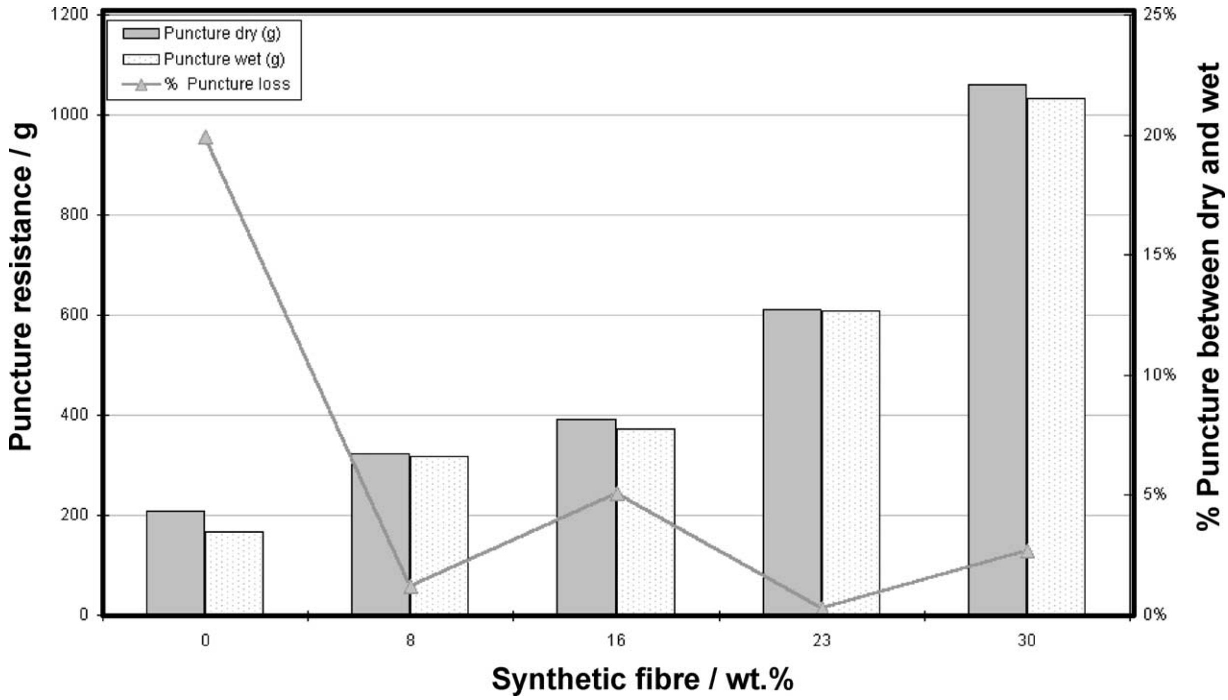

Fig. 4. Puncture resistance dry and wet.

rator is mechanically stressed, particularly if the machines are highly automated. As previously described, the synthetic fibre enhances the tensile strength and reduces any difficulty due to separator weakness. When the plates are stacked with AGM separators and then pressed into battery cases, dry punctures can occur on the edges of the plates and can cause short-circuits in the subsequent battery processing. This typical puncture problem is illustrated in Fig. 6.

3.3.2. Battery life

During cycle-life, plate volume tends to change depending on charge and discharge states. AGM, as an elastic material, is able to follow these changes during cycling. If the plate

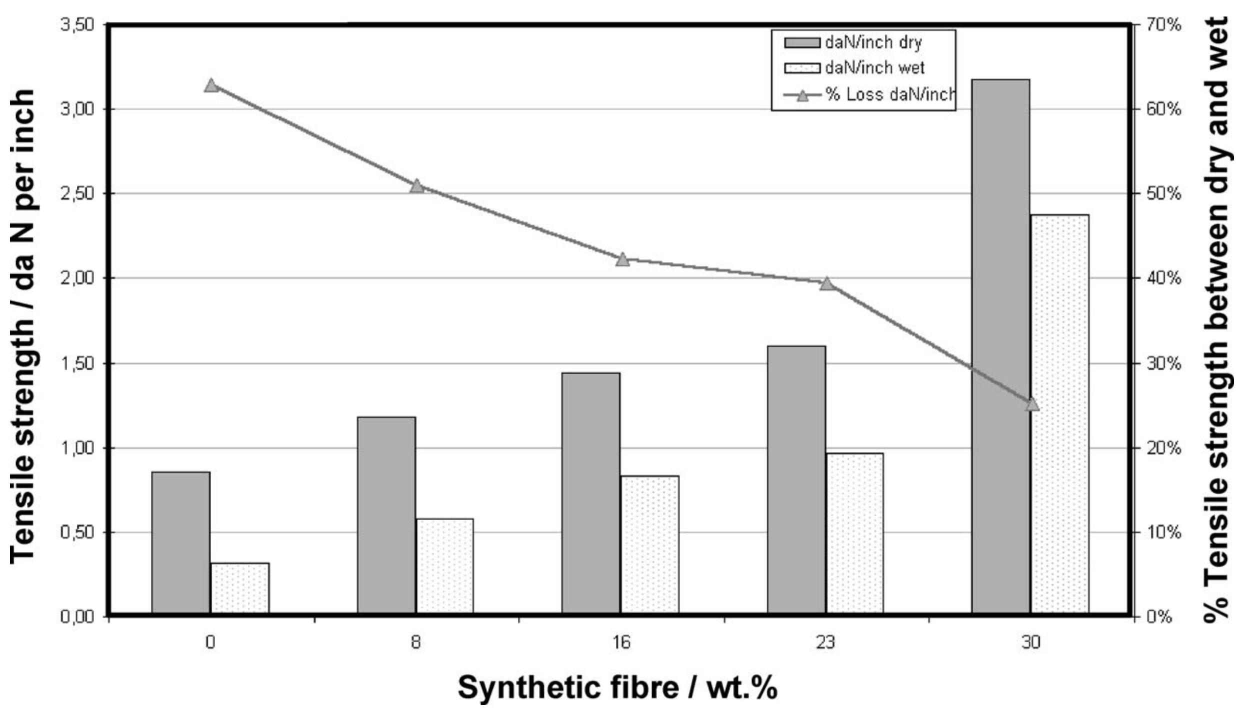

Fig. 5. Tensile strength dry and wet.

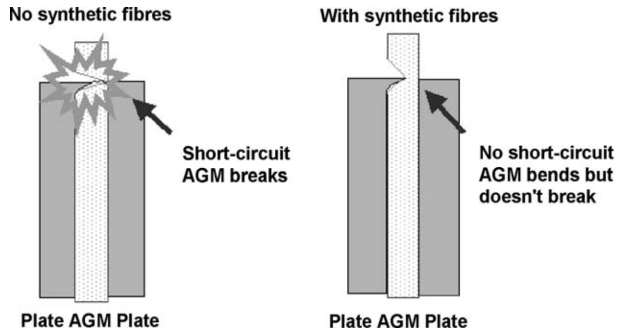

Fig. 6. Puncture short-circuit during assembling.

surfaces are not sufficiently smooth, irregularities can create compressed zones where plates are occupying their greatest volume. In these zones, the AGM structure is mechanically stressed: (i) 'compressed' where there is a 'bump'; (ii) 'stretched' around this 'bump'.

Without synthetic fibre reinforcement, the stretched zone makes an irreversibly more open structure, which is more prone to suffer short-circuits. With synthetic fibre reinforcement, these stretching zones are held together firmly by the fibre structure. This phenomenon is illustrated in Fig. 7.

3.3.3. *Bernard DUMAS AGM separators: RECOMAT®*

The standard 100% glass separators made by Bernard DUMAS are classified mainly by their specific surface area (SSA), which ranges from 0.9 to 1.45 $m^2\,g^{-1}$. A product range has been created by adding some synthetic fibres to the standard separators in order to improve the properties. Due to this synthetic fibre addition, the standard products have been reinforced both for puncture and for tensile strength (see Tables 1 and 2). As a consequence, the separators made of RECOMAT® 16,000, 15,000 and 17,000 will have better resistance to short-circuits and to dendrite formation than will those of the all-glass materials B3000, 2000 and 7000.

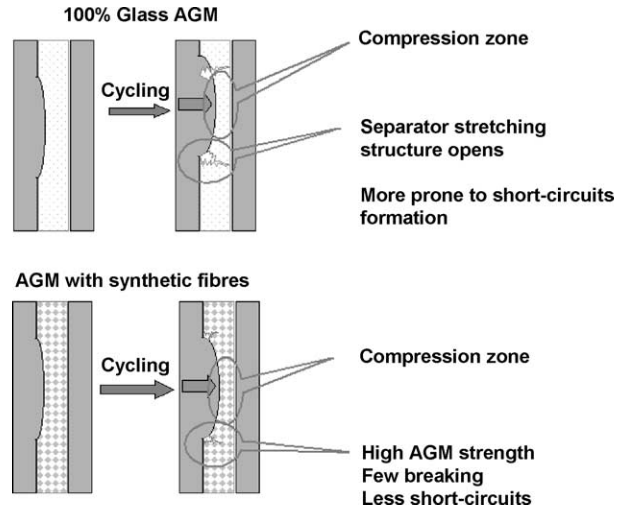

Fig. 7. Puncture short-circuit during cycle-life.

Moreover, process ability will be improved by using these reinforced separators.

4. Internal pressure testing—fatigue test under cycling

During battery assembly, the AGM separator is first compressed between the plates in the dry state. The compressed stacks are then pushed into the case. After welding and closing the battery, sulphuric acid is added.

During battery life, the plates change in volume depending on the chemical state of the active material. When lead and lead oxide are converted to lead sulphates, there is an increase in volume, which compresses the separators trapped in between. The separator is compressed and relaxed according to the state-of-charge of the battery.

In order to understand better the impact of synthetic fibre on internal battery pressure, two tests have been developed

Table 1
Typical AGM separator puncture resistance

Specific surface area ($m^2\,g^{-1}$)	Separator name (100% glass material) RECOMAT®	Puncture resistance with 100% glass material (g for 250 $g\,m^{-2}$)	Separator name, new range with 8 wt.% synthetic fibre, RECOMAT®	Puncture resistance with 8 wt.% synthetic fibre (g for 250 $g\,m^{-2}$)	Improvement (%)
0.9	B3000	590	16000	750	+27
1.1	2000	620	15000	820	+32
1.45	7000	670	17000	1030	+54

Table 2
Typical AGM separator tensile strength

Specific surface area ($m^{-2}\,g^{-1}$)	Separator name (100% glass material) RECOMAT®	Tensile strength (daN $in.^{-1}$ for 250 $g\,m^{-2}$)	Separator name, new range with 8 wt.% synthetic fibre, RECOMAT®	Tensile strength with 8 wt.% synthetic fibre (daN $in.^{-1}$ for 250 $g\,m^{-2}$)	Improvement (%)
0.9	B3000	1.4	16000	1.7	+22
1.1	2000	1.9	15000	2.5	+32
1.45	7000	2.4	17000	3.0	+25

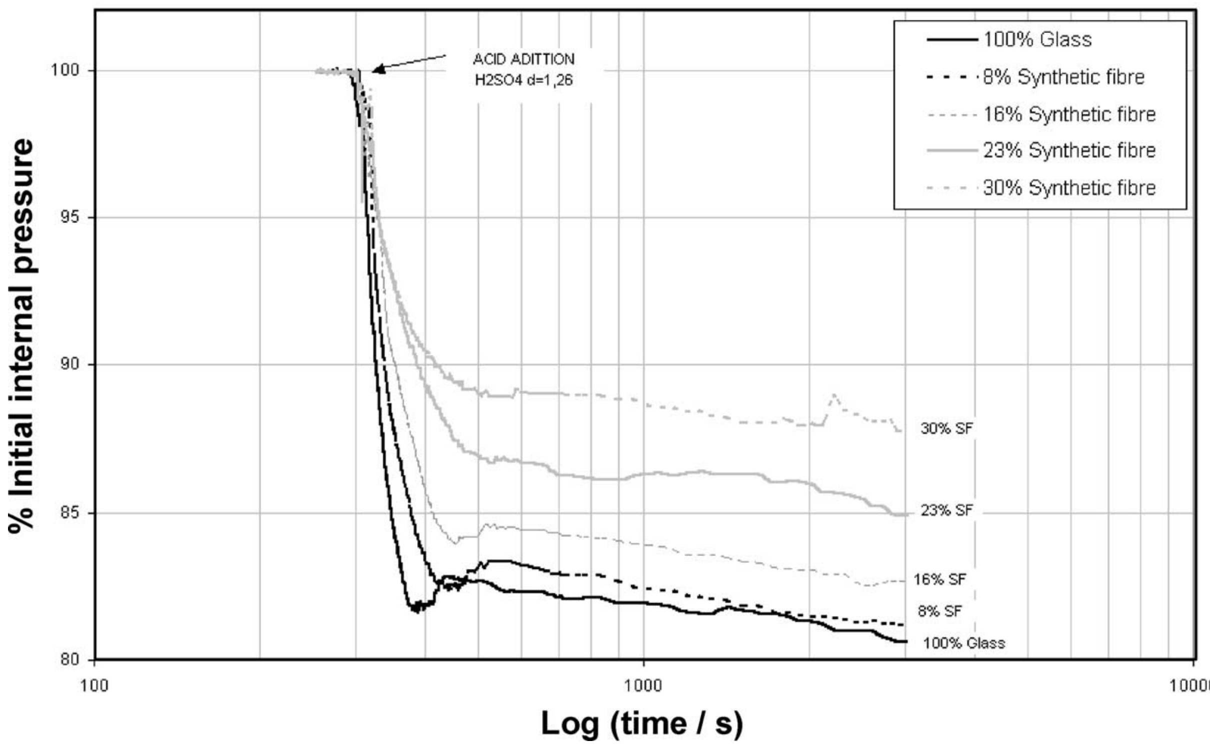

Fig. 8. Internal pressure loss when acid is added.

to follow and simulate these steps of battery construction and life, namely (i) dry compression and acid filling (see Section 4.1); (ii) compression cycles (fatigue test) (see Section 4.2).

4.1. Internal pressure behaviour

In order to follow the internal pressure, a piston cell has been constructed. This is able to set any desired applied pressure on a 100 cm^2 square separator sample. When studying internal pressure, dry pressure is first applied and the separator is allowed to stabilize for a few minutes. The thickness is then fixed with screws and acid is added to the separator up to near 100% saturation. As the thickness is fixed, sensors measure only the change in internal pressure. The percentage of initial internal pressure with time is recorded as shown in Fig. 8.

When acid is added, the pressure drops down very quickly. As acid penetrates the pores, the AGM has less capacity to resist external pressure. Acid penetration creates two major effects: (i) capillary forces inside each pore decrease, creating an overall internal pressure drop; (ii) acid wets the points of contact between the fibres and makes them more able to move and reorganize.

When synthetic fibres are added and melted to a large amount of glass fibres, the reorganization effect inside the AGM is reduced so internal pressure can decrease less. The greater the number of synthetic fibres, the less the fibres can move in the AGM and the less is the loss of pressure (Fig. 8).

4.2. Compression cycle (fatigue test)

During battery cycling, the space available for the AGM separator changes due to the change in volume of the plate active-material, as mentioned above. The AGM must follow these changes in order to maintain a good contact between the plates and the electrolyte trapped in the AGM. Therefore, it must have maximum elastic recovery during cycling, to guarantee a good capacity throughout battery life.

The purpose of this study is to measure AGM behaviour during these cycling changes in volume. This test measures the elastic recovery of the AGM, not only after one cycle but after several pressure cycles. One layer of AGM is placed in the piston described earlier and the internal pressure is cycled between 10 and 50 kPa every 180 s. The thickness is recorded during this cycling and gives the plot showed in Fig. 9.

From the type of data shown in Fig. 9, the maximum thickness of each cycle at 10 kPa is taken as the recovery thickness of each cycle. The elastic recovery in % can then be calculated as the ratio between the instantaneous thickness at 10 kPa over the initial thickness before cycling at 10 kPa. This elastic recovery can be plotted as a linear function of the logarithm of time, as shown in Fig. 10. The elastic recovery after 1 and 20 cycles can be plotted and AGM with different amounts of synthetic fibres can be compared, both in dry and humid wet states (Fig. 11). It is seen that the greater the amount of synthetic fibre that is reinforcing the

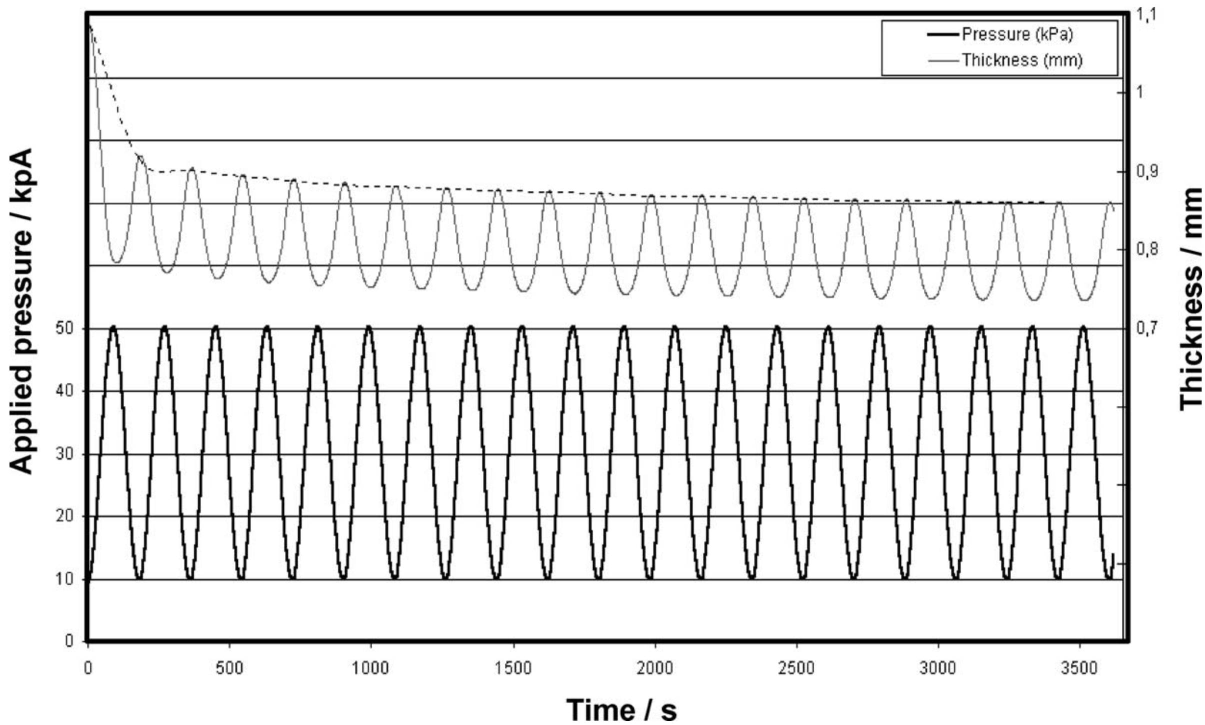

Fig. 9. Example of fatigue test: 20 compression cycles.

AGM, the better is the elastic recovery in both the dry and the wet states. Again, the more tightly are the glass fibres bound together, the more stable is the fibre structure and so the elasticity is improved.

In most cases, elasticity is better in the wet state than in the dry state. This can be explained by the fact that in the wet state the fibres can move more easily and reorganize, so more reversible effects are possible. On the other hand, in

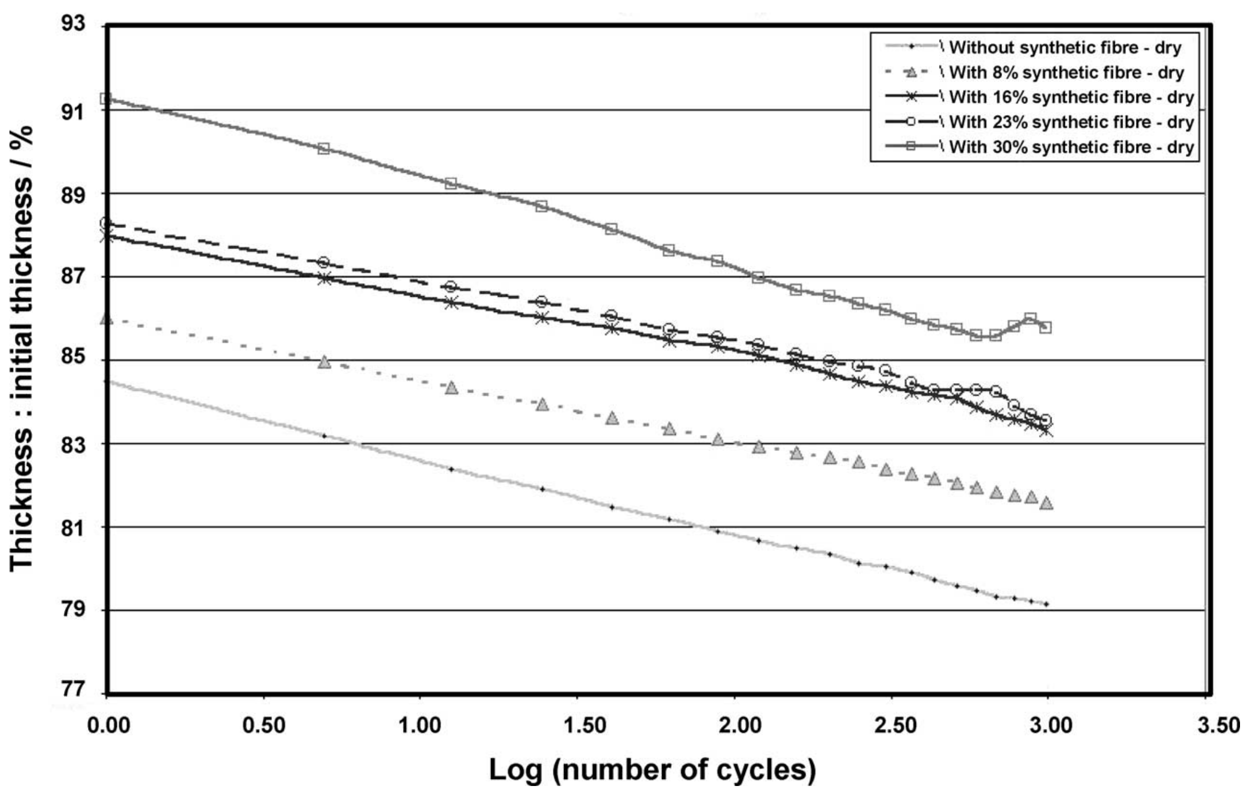

Fig. 10. Elastic recovery after compression cycling.

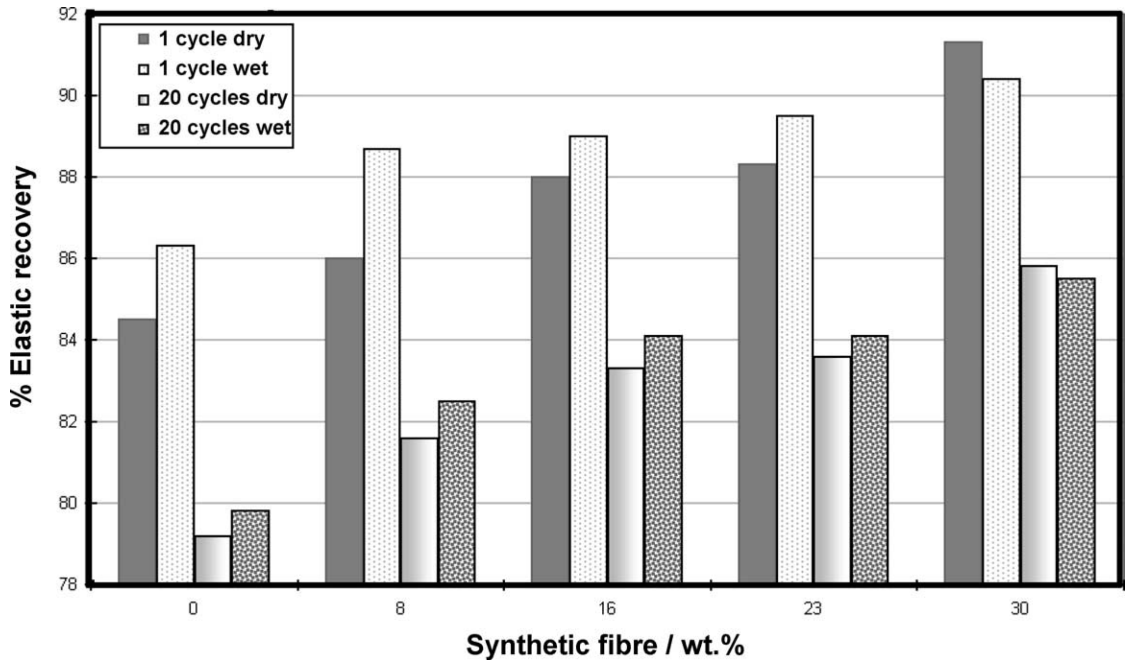

Fig. 11. Elastic recovery after 1 and 20 cycles: dry and wet.

the dry state, since the fibres have less possibility to move, when pressure is applied, more irreversible fibre breakage occurs and results in less elasticity.

5. Side effect of synthetic fibres

As demonstrated, synthetic fibre addition brings many advantages to AGM separators, but organic fibres can also have some side-effects that have to be mentioned here:

- *Pore structure*. Synthetic fibres are large compared with glass fibres (>11 μm diameter versus less than 1 μm for most glass microfibres). This large size can have an impact on pore structure when a large amount of organic fibre is added. Up to 10 wt.%, synthetic fibre has little impact on the pore structure, but with higher percentages the change in pore structure can have some negative effects on capillary rise and stratification.
- *Welding*. AGM reinforced with synthetic fibre can be welded by ultrasonics, heat, or a mechanical tool. Thus, it is possible to use sealed envelopes around the plates. Traditionally, more than 20 wt.% of synthetic fibre is needed, but recently some battery manufacturers have managed to build separator envelopes with only 8% of synthetic fibres.
- *AGM cutting*. When these new products are used on standard VRLA battery lines, knives that cut 100% glass have to be set slightly differently, with stronger pressure, in order to make clean cuts.
- *Separator wetting*. Glass has very good wettability with sulphuric acid. Organic fibre, depending on the chemistry used, has less affinity for sulphuric acid but still has very good wettability. This very slight decrease of wettability has a minor impact on overall separator wettability because the surface area of the synthetic fibre added is very small compared with the surface area provided by the micro-glass fibre. In fact, 8 wt.% of synthetic fibre ($0.05\,m^2\,g^{-1}$ specific surface area) in an AGM having $1\,m^2\,g^{-1}$, will represent only 0.4% of the total specific surface area. For high amounts of synthetic fibre (more than 15%), wettability starts to be affected.

6. Conclusions

The addition of synthetic fibres into an AGM separator significantly improves the mechanical characteristics. These organic fibres bind glass fibres and help to keep internal pressure in the glass mat higher when acid is added, and to ensure superior elastic recovery during cycling. As a consequence, using reinforced separators in VRLA batteries will:

- increase the process efficiency,
- lower the scrap level of battery assembling lines,
- improve battery performance (higher internal pressure and better electrolyte/plate contact during battery life).

The amount of synthetic fibre to be added to any separator has to be optimized in order to find the best compromise between improving the properties described here and maintaining the advantages of very fine glass microfibres.

Experience in the battery market has shown that with 8 wt.% of synthetic fibre reinforced separators, only positive effects are recorded, both on assembly lines and with battery life.