

New generation of non-woven gauntlets for tubular positive plates

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Abstract

The efficiency of non-woven gauntlets for tubular positive plates in industrial lead acid batteries is well known, both in terms of cost and performance. In order to be even better suited for the most demanding applications and filling processes, the non-woven gauntlet properties have been further improved thanks to an extensive work on the fabric itself and on the forming process. As a result, a complete range of non-woven gauntlets are nowadays available depending on the battery type, filling method and end-use: beside the standard and reinforced point-bonded Polyethylene Terephthalate (PET) fabrics, also available with edge insulation, a brand new gauntlet type has been especially developed for stationary and gel VRLA batteries. The new generation of gauntlets is based on a flat calendered bicomponent non-woven fabric. This bicomponent material has two main advantages, which are normally antagonist in the point-bonded fabric technology: improved mechanical strength and elasticity in combination with a reduced electrical resistance. A patent is pending for this new generation of non-woven gauntlets.

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1. Introduction

The positive tubular plate has been used in industrial lead-acid batteries for almost a century now. The tubular plate design, based on cylindrical tubes and spines, presents a series of advantages over the flat plate design, especially improved specific energy (Wh kg^{-1}), improved energy density (Wh l^{-1}), and higher positive active mass (PAM)/grid ratio.

From the early 1950s up to now, the tubular plate has evolved from the single tube design (PVC tubes first, then woven or braided tubes of C-glass fibers protected by a perforated plastic armor, or impregnated with a phenolic resin like in Fig. 1a) to the more economical and productive multitube gauntlet concept. The first generation of gauntlets, still in use for some applications, have been made of woven polyester fabric initially impregnated with phenolic resin and more recently with thermoplastic acrylic resin (Fig. 1b) [1]. Since the 1980s, the tubular gauntlet has further evolved to include thermo-formed non-woven fabrics. Contrary to the previous woven technology, the possibility to form these new materials into various tube shapes (not only round, but also square, rectangular or elliptic), allows battery manufacturers to overcome the main weaknesses

of the tubular plate technology and to extend its use to new applications like electric vehicle and photovoltaic battery applications: the lower power output and charge acceptance due to the reduced contact surface between the PAM and the spine have been overcome by the use of strap grid tubular plates (SGTP) and elliptic non-woven gauntlets [2].

Up to the recent years, only point bonded polyester spun-bond fabrics were used to form non-woven gauntlets (Fig. 1c). This standard original fabric has evolved through reinforced versions, also including options like the edge insulation, in order to be even better suited for more demanding applications and filling methods. However, despite the improvements made on the point-bonded fabric type, the material inner properties presents some intrinsic limitations. In order to further push the non-woven gauntlets performances, some new material types like flat calendered bicomponent fabrics have been investigated, the target being to expand the use of non-woven gauntlets into the latest battery designs, including stationary and valve-regulated batteries.

2. Performance of standard point-bonded polyester non-woven fabrics

It is nowadays well admitted that, beside the substantial cost reduction over their woven counterpart, non-woven gauntlets (traditionally made of point-bonded polyester non-woven fabric) offer real technological benefits, which help raise the quality

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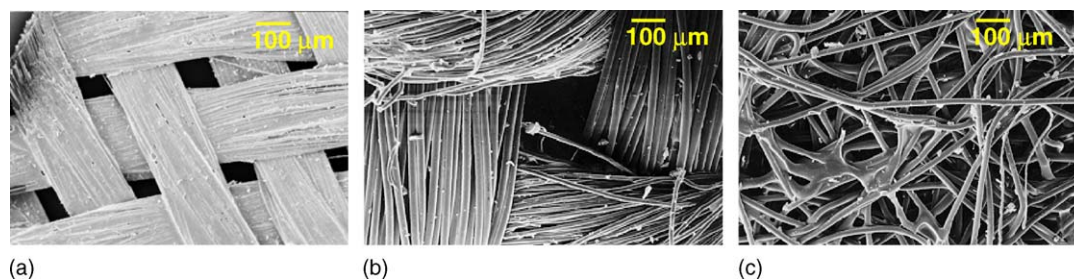


Fig. 1. Scanning electron microscope pictures of (a) glass tube, (b) woven fabric and (c) non-woven fabric, with a magnitude of $\times 100$.

and performance of the tubular positive plates [3,4]. Their higher efficiency is mainly due to the fabric physical properties. Table 1 gives some reference numbers on porosity and acid retention. As mentioned, the overall pore volume of non-woven mats is around 70%, which is much higher than the 40% reached by the woven fabrics. Also the pore size distribution is different, with lower pore size for the non-woven fabric (mean pore size around $30\ \mu\text{m}$ compared to $100\ \mu\text{m}$ for the woven type), mainly due to the random filament deposition on the conveyor belt during the spunbond mat manufacturing process. The different pore structure, and especially higher pore volume associated with lower pore size for non-woven fabrics leads to a better fluid management, and especially a higher ability to absorb and retain the electrolyte inside the pores, thanks to higher capillary forces: it has been measured that an average $0.12\ \text{g cm}^{-2}$ acid is absorbed inside the non-woven fabric pore structure, while only $0.05\ \text{g cm}^{-2}$ stays in the woven material. This phenomenon leads to improved ionic exchanges through the fabric wall, and consequently to reduced electrical resistance of fabric. As a result, the electrical resistance of the non-woven gauntlet itself is also very much reduced, leading to lower cell internal resistance and higher battery capacity.

Reduction of the electrical resistance is not the only consequence of the different microscopic structure of both types of fabrics. The lower pore size of the non-woven fabrics has a beneficial impact also later in life, thanks to the greater ability of the mat to retain small crystals. It is actually recognized that the positive active material suffers degradation when repeated charge/discharge cycles occur, because the alternating dissolution and precipitation processes convert the agglomerated initial paste structure into an accumulation of fine crystals. This process known as “shedding” is responsible for the loss of active mass through the gauntlets walls. On weighing the shed active mass accumulated at the bottom of cells after cycling, it has been found that the deposit is 1/3 reduced with non-woven gauntlets due to the finer pore structure of the fabric. The importance of

Table 1
Comparison between standard non-woven fabric (PB1) and woven fabric—main physical properties (mean values)

	Woven fabric	Standard non-woven fabric (PB1)
Mean pore size (mm)	>100	30
Volume porosity (%)	40	70
Acid absorbed (g cm^{-2})	0.05	0.12

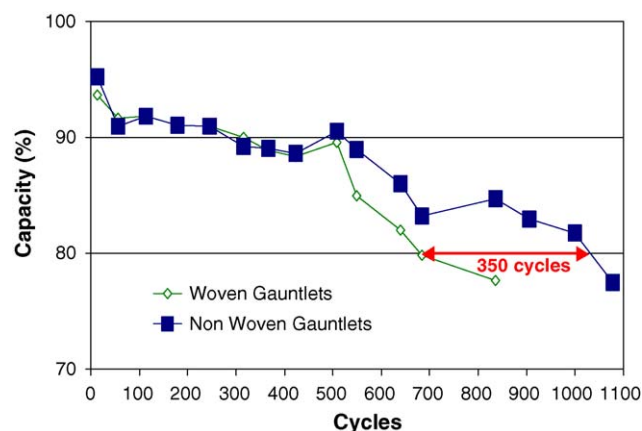


Fig. 2. Accelerated life cycle test results of traction cells using woven and non-woven gauntlets made of polyester spunbond point-bonded fabric.

keeping fine crystals inside the tubes had already been outlined elsewhere, as they also act as binders to the positive active material, hence increasing performance and cycle life [5,6]. Fig. 2 clearly shows the benefit of a better active mass retention inside the non-woven gauntlets, as 1100 accelerated cycles have been performed with non-woven gauntlets compared to only 700 with the woven gauntlets on flooded traction cells (Tables 2 and 3).

Table 2
Comparison between standard non-woven and woven fabrics and gauntlets properties—general trends

	Woven standard non-woven (PB1)
Fabric	
Volume porosity	Lower
Pore size	Higher
Air permeability	Lower
Amount of acid absorbed	Lower
Amount of acid retained	Lower
Electrical resistance	Higher
Tensile strength MD and CD	Higher ^a
Elongation MD and CD	Lower ^a
Gauntlets	
Active mass shedding	Higher
Active mass retention	Lower
Electrical resistance	Higher
Mechanical strength	Higher ^a
Elastic modulus	Better ^a
Battery capacity and cycle life	Lower
Price	Higher

^a Improved with the new fabric type.

Table 3
Physical properties of standard point bonded non woven fabric (PB1), and reinforced point bonded fabric (PB2, PB3) and new flat calendered bicomponent fabric (New FC)

		PB1	PB2	PB3	New FC
Fabric properties (typical values)					
Tensile strength MD	N/5 cm	433	552	460	549
Tensile strength CD	N/5 cm	375	546	430	435
Elongation MD	%	28.2	33.9	25.1	35.8
Elongation CD	%	33.7	34.5	22.8	23.1
Electrical resistance	mΩ cm ²	75	160	90	70
Air permeability	l/m ² s	1030	564	810	950
Pore volume	%	74.6	64.5	69.5	71.6
Gauntlets properties (typical values)					
Burst strength	bars	13.6	16.7	17.5	19.5
Electrical resistance	mΩ cm ²	185	295	206	175

Table 4
Physical properties of PVC microporous separators compared to PE and PE/rubber

Typical values	Ribbed PVC/silica	Corrugated PVC/silica	PE	PE/rubber
Thickness (mm)	2.0	2.0	2.0	2.10
Backweb (mm)	0.50	0.57	0.50	0.45
Total porosity (cm ³ g ⁻¹)	1.20	1.58	0.90	0.73
Pore volume (%)	68	73.9	55	49
Electrical resistance (mΩ cm ⁻²)	130	80	200	270
Acid displacement (ml m ⁻²)	300	180	300	390
Wettability (s)	+++	+++	–	–

Generally speaking, the decrease of capacity is not the only consequence of the active mass passing through the gauntlets. Short circuit may also occur due to lateral mousing. Up to now, the only way to overcome this phenomenon was to wrap the negative plate in polyethylene-based separator sleeves. However, the performance of this type of separators is reduced compared to highly porous PVC/silica ribbed or corrugated leaf type separators, mainly due to their lower pore volume and consequent higher electrical resistance and acid displacement (Table 4) [7,8]. In order to be able to get rid of the sleeve and use higher quality microporous separators, while avoiding lateral shorts, the insulation of the non-woven gauntlets edges has been developed. The protection is made by the application of hotmelt all along both outside tubes. The fine resin layer covers less than half both external tubes, so that the capacity loss is negligible (Fig. 3).

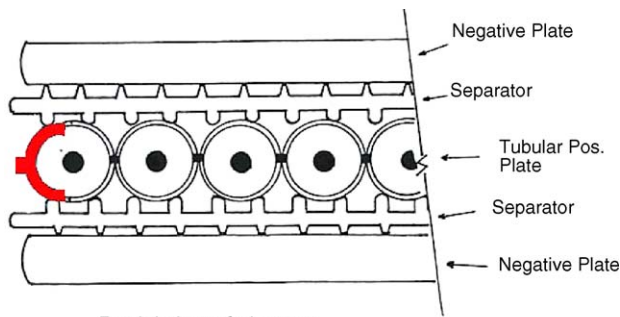


Fig. 3. Partial view of element insulated with leaf type ribbed separators and non-woven gauntlets (PET point-bonded spunbond) with hot-melt edge protection.

Battery life cycle testing performed on 3PzS240 traction cells insulated with leaf type separators have shown that the cell assembled with gauntlets without edge protection failed after 1000 cycles, while both cells insulated with leaf type separators but using non-woven gauntlets with edge protection are still running after 1550 cycles (Fig. 4). It is also clear, based on the picture attached to Fig. 4, that the premature failure was due to short circuit caused by lateral mousing.

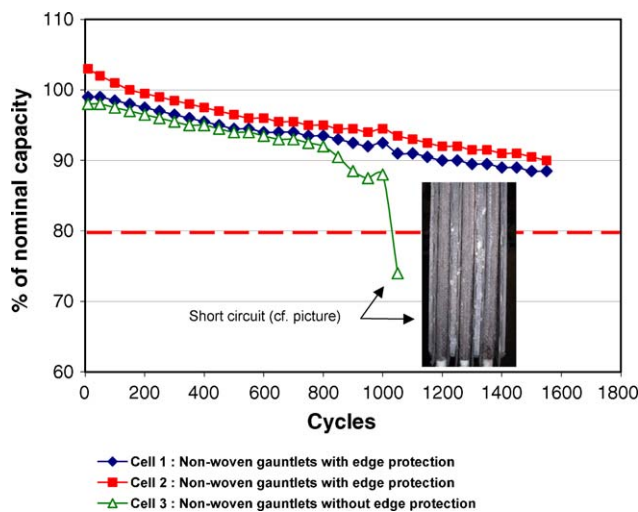


Fig. 4. Life cycle test comparison of two traction cells insulated with non-woven gauntlets with lateral insulation compared to one traction cell insulated with non-woven gauntlets without edge protection. Both gauntlets types are made with point bonded spunbond PET fabric.

Surprisingly however, despite the performance and cost advantage of non-woven gauntlets based on polyester spun-bond flat calendered fabrics, some battery manufacturers are still reluctant to use them as a replacement for woven gauntlets for certain type of batteries (like stationary flooded or gel batteries) or filling processes. This is not entirely due to excessive caution or a certain reluctance for changes. More objective justifications can be found in the weaker mechanical properties of standard point-bonded non-woven gauntlets, as summarized in Table 1. That is the main reason why a new generation of gauntlets (referred as New FC in the different tables and figures) based on a different non-woven fabric technology has been developed. The target was to fill this gap in terms of mechanical and elastic properties, while keeping the advantages of non-woven fabrics in terms of electrical performance and cost. The following paragraphs will demonstrate that the goal has been reached.

3. New generation of non-woven gauntlets: a big step forward in the combination of electrical/mechanical/cost performance

The gauntlets mechanical properties (burst strength, tube expansion under pressure and elasticity) play an important role at different stages of the battery life, and first, during the filling operation, which is the key process in the production of tubular positive plates [9–12].

Four different filling techniques are still used [11]:

- (1) Dry filling with lead oxide powder, where the tubular plate comprising spines inserted in the gauntlets tubes are placed into the vibration (or shaking) chamber of a filling machine to be filled with dry lead powder (leady oxide), then immersed in sulfuric acid, dried and subjected to formation.
- (2) Wet filling with water suspension of a mixture of lead powder (leady oxide) and red lead, where both oxide types are mixed in the dry stage, and then mixed with water to reach a defined density. The tubes of the tubular plates are then filled under pressure with this suspension, treated with sulfuric acid (pickling), washed, dried and subjected to formation.
- (3) Wet filling with a suspension of paste, where the paste is produced first with sulfuric acid, water being added afterwards to reach a definite suspension density, with which the tubes are filled under pressure. After filling, the plates are subjected to curing and subsequent formation.
- (4) Filling with paste, where paste is produced first and injected under pressure into the gauntlets tubes, before curing and formation.

In dry filling, the gauntlet fabric has to have a high air permeability in order to allow the air displaced by the incoming oxide powder to be efficiently evacuated from the tubes through its porous structure. Both standard point-bonded fabric (referred as PB1 in Table 3) and the new flat calendered bicomponent fabric (referred as New FC in Table 3) have a higher air permeability than woven fabric (measured around $800 \text{ l m}^{-2} \text{ s}^{-1}$), due to their higher pore volume.

Additionally, it is also important that the internal surface of the tubes is smooth enough for the lead powder to overcome the minimum resistance when filled into the tube. Contrary to most conventional standard point-bonded non-woven fabrics, the new flat calendered bicomponent fabric has a flat and smooth surface with no hair inside, which enables an easy and efficient dry filling.

The wet filling method requires that the gauntlets act as a filter retaining all the solid particles and allowing the excess liquid to flow through. Since the finest particles in the filling slurry can measure only a few microns across, the advantages of a fine and uniform porous structure are evident. This is the case for both non-woven fabric types (PB1 and new FC). However, the new FC fabric might be even more efficient as its surface does not present the calender prints of the point bonding where the polyester filament are melted, and therefore 100% of its surface can participate to the filtration operation.

Filling with paste is realized under different pressure depending on the equipment (Hadi or Hoppecke machine). With standard PB1 point-bonded fabrics, the use of high pressure for paste filling has to be restricted to a certain level in order to avoid the tubes destruction. As mentioned in Table 3, the tensile strength of the PB1 fabric in the machine direction is in the 430 N/5 cm range and 375 N/5 cm in the cross direction, leading to gauntlets burst strength at about 14 bars.

A possible improvement of the point-bonded standard fabric PB1 consists on mechanically reinforcing the fabric through a modification of its composition (samples referred as PB2 and PB3), while keeping the thickness in an acceptable range to be able to reach the gauntlets final dimension. The improvement of the tensile strength is effective for both PB2 and PB3 fabric. However, the impact on the gauntlets properties is not fully satisfactory: while the burst strength increases up to 16.7 and 17.5 bars for PB2 and PB3, respectively, the electrical resistance unfortunately also increases significantly up to 295 and 206 $\text{m}\Omega \text{ cm}^2$, respectively, compared to 185 $\text{m}\Omega \text{ cm}^2$ for the standard PB1 fabric.

The properties of the new polyester flat calendered fabric (referred as New FC) are summarized in Table 3. Compared to PB1, only the machine direction (MD) and cross direction (CD) tensile strength have been improved. However, because the product cohesion is not due to melted areas (point bonding), the behavior during gauntlets formation as well as the final properties of the gauntlets are totally different. Not only the burst strength of the gauntlets is much higher (19.5 bars), but the electrical resistance is surprisingly low (only 175 $\text{m}\Omega \text{ cm}^2$), even compared to gauntlets made with the standard material PB1. These enhancements in the performance could not have been foreseen from the physical properties of the starting material and this is the first time that both the mechanical and electrical properties have been improved simultaneously. This might be explained by the fact that the ionic exchanges are possible over all the product surface area, while only the non-bonded areas can efficiently be impregnated with electrolyte and participate to the ionic exchanges in the case of point-bonded fabrics. The technical gap is represented in Fig. 5. As a result, the new FC fabric allows the new generation of non-

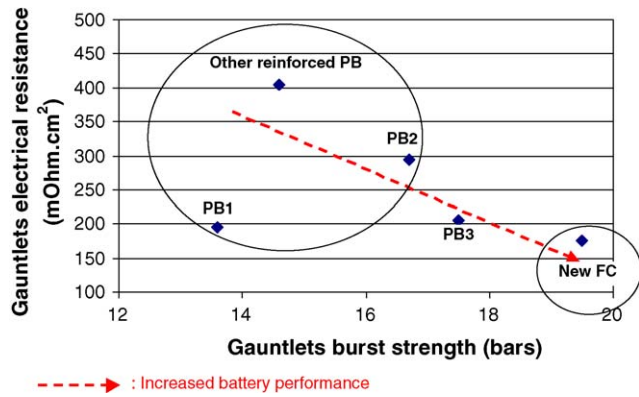


Fig. 5. Electrical resistance versus burst strength for gauntlets made with standard and reinforced point-bonded non-woven fabrics (PB labels) compared to the new bicomponent flat-calendered non-woven fabric (New FC). Illustration of the technical gap.

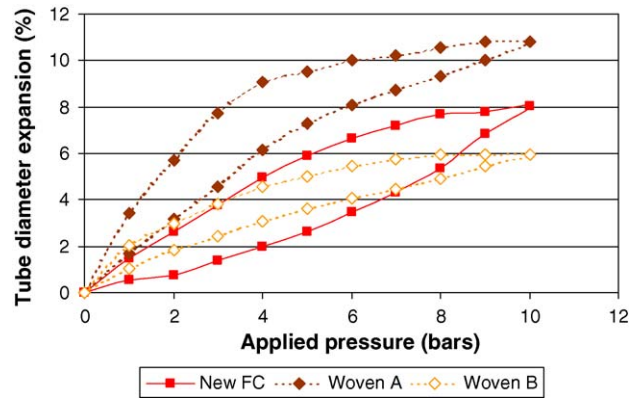


Fig. 7. Mechanical properties of gauntlets made with the new FC non-woven fabric compared to two different widely used woven gauntlets (Woven A and Woven B)—Tube diameter expansion vs. increasing and decreasing internal pressure load.

woven gauntlets to be efficiently filled by any of the existing methods.

More importantly and besides the critical filling operation, the mechanical and elastic properties of the gauntlets are crucial parameters mainly during the battery life, as the positive active mass undergoes volume changes during alternate charges and discharges due to the transformation of PbO₂ into PbSO₄ and vice versa. This phenomenon is known as active mass “breathing”. The gauntlet has not only to limit the plate expansion during discharge, but also be elastic enough to perfectly constrain the active mass during its subsequent contraction on recharge. This is the only way to ensure the permanent cohesion of the active mass particles among themselves and around the lead spine in order to avoid shedding and premature capacity loss. Figs. 6–10 illustrate the mechanical and elastic properties of the new generation of non-woven gauntlets made of flat calendered bicomponent fabric compared to standard and reinforced point-bonded non-woven gauntlets and to two types of woven gauntlets.

The first test (Figs. 6–8) consists on inserting a rubber tube inside the gauntlet and to change the internal pressure from 0

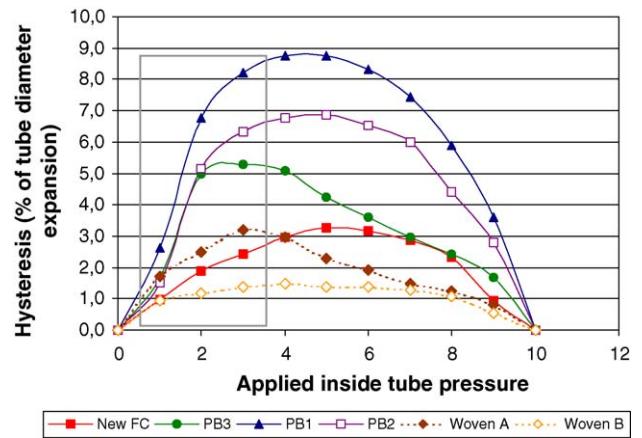


Fig. 8. Elastic properties of gauntlets made with different types of non-woven fabrics (PB1: standard PET point-bonded fabric, PB2 and PB3: reinforced point bonded fabrics, New FC: flat calendered bicomponent fabric)—Hysteresis on tube diameter between increasing and decreasing pressure at each pressure load between 0 and 10 bars (derived from Fig. 4a).

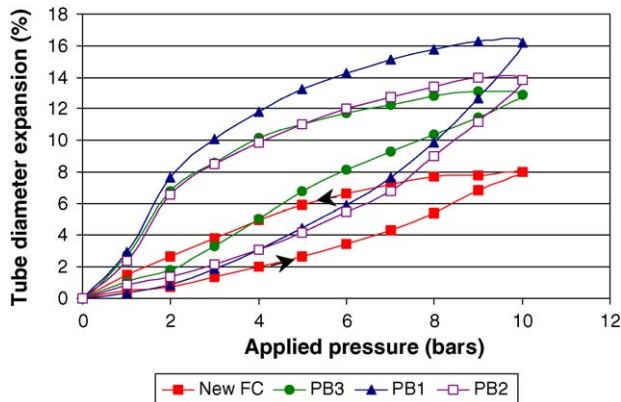


Fig. 6. Mechanical properties of gauntlets made with different types of non-woven fabrics (PB1: standard PET point-bonded fabric, PB2 and PB3: reinforced point bonded fabrics, New FC: flat calendered bicomponent fabric)—Tube diameter expansion vs. increasing and decreasing internal pressure load.

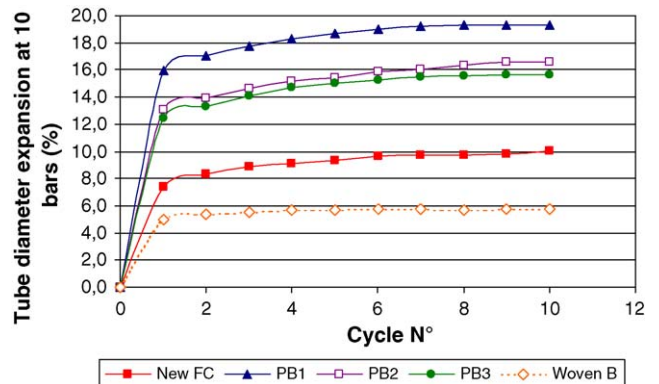


Fig. 9. Gauntlets elastic properties. Tube submitted to 10 successive expansions from 0 to 10 bars (simulation of positive active mass breathing). Comparison between different types of non-woven fabrics (PB1: standard PET point-bonded fabric, PB2 and PB3: reinforced point bonded fabrics, New FC: flat calendered bicomponent fabric) in comparison with woven fabric.

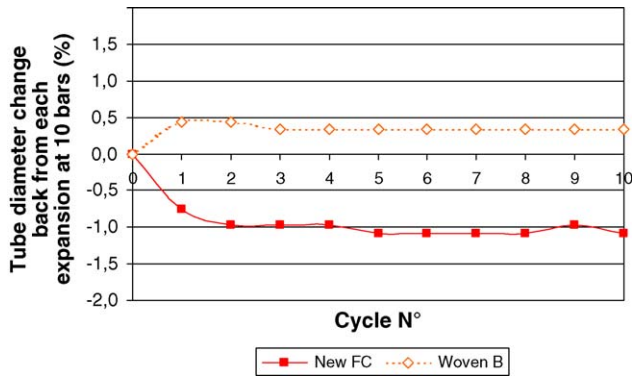


Fig. 10. Mechanical properties of the new generation of non-woven gauntlets made with flat calendered bicomponent non-woven fabric compared to woven fabric: tube diameter changes when internal pressure is back to 0 after successive expansions at 10 bars (simulation of positive active mass breathing).

to 10 bars and back to 0 bar by increments of 1 bars. At each pressure step, the outside tube diameter is measured and the expansion is calculated based on the initial tube diameter. Fig. 6 compares the behaviour of the new type of gauntlets (new FC) with standard and reinforced non-woven gauntlets. Standard gauntlets tubes (PB1) generally increase regularly under pressure and reach around 16% diameter expansion at 10 bars. Moreover, when decreasing pressure, the tube diameter measured at each step while coming back is much higher than the diameter measured while going up. This may simulate the limited ability of this type of non-woven gauntlets to constrain efficiently the positive mass during breathing.

The reinforced point-bonded materials PB2 and PB3 show an improved behaviour, as only 12–14% are reached at 10 bars, and also because the difference in tube diameter measured at each step while comparing increasing and decreasing pressure is reduced. This thinner hysteresis is better illustrated in Fig. 8, which has been directly derived from Fig. 6 by calculating the percent tube expansion difference at each pressure step between increasing and decreasing pressure. While the difference is in the order of 2.5–9% for PB1 fabric type, they are reduced to 1.5–7% for PB2 and 1.5–5.5% for PB3.

In that extent, the reinforced products PB2 and PB3 already represent an improvement compared to the standard PB1 version. However, this small step ahead has nothing to do with the more impressive improvement achieved with the new generation of gauntlets (new FC). Fig. 6 shows that the tube diameter expansion reaches only about 8% at 10 bars, which places the new generation of non-woven gauntlets at a level of performance comparable to their woven counterparts, in terms of tube deformation. This is better represented in Fig. 7, where two types of woven gauntlets have been measured for comparison: the tube diameter expansion for the woven gauntlets reaches 11 and 6% for woven type A and B, respectively.

The hysteresis measured on woven gauntlets type A is also very good, as differences in the range of 0.5–1.5% only have been measured. Woven gauntlets type B are not so good with an hysteresis reaching 3.2% at 3 bars. The difference measured on

both woven types is due to the various quality of woven gauntlets available on the market depending on the type of filament used. It is well known that the (spin-yarn/filament-yarn) ratio can vary and be increased in the benefit of the less robust one for cost reasons, with the consequent deleterious impact on the mechanical and elastic properties of the gauntlets. Moreover, as spinning directly influences the filaments' crystallinity (ratio between the amorphous and crystalline zones), the chemical resistance of woven gauntlets to oxidation may also be affected. That is the main reason why the new flat calendered bicomponent fabric has been manufactured with the best parameters possible for the spunbond technology and a quite high filament denier in order to improve the oxidation resistance of the new generation of gauntlets and make them more suitable for long term guarantee applications like stationary batteries.

Coming back to the mechanical testing, the values of the hysteresis between 1 and 3 bars for each type of gauntlets (gray frame in Fig. 8) have to be further commented. They illustrate the elastic properties and the ability of the gauntlets to constrain the positive active mass at the end of the retraction, when it is the more crucial that the cohesion between the particles is ensured. As shown in Fig. 8, the difference in tube diameter expansion between increasing and decreasing pressure at 1–3 bars ranges from 1 to 2.5% for the new FC gauntlets, which is intermediate between both woven gauntlets performance and much better than the other non woven gauntlets types.

More precisely, the elastic characteristics of the various gauntlet types have been studied with a second test, where the tube diameter has been measured (i) after 10 successive pressure increases from 0 to 10 bars (Fig. 9) and (ii) when the pressure has been released back to 0 in the following sequence: 0-10-0-10-0-10 ... (Fig. 10). In both figures one cycle represents a single increase to 10 bars with subsequent decrease to 0 bar internal tube pressure. Fig. 9 shows that standard and reinforced non-woven gauntlets PB1, PB2 and PB3, stabilize at values around 19.5, 16.5 and 15.5% tube expansion, respectively, after several successive expansion cycles, while the new FC gauntlets reaches only 10%, which is much closer to the behaviour of the best woven gauntlet (type B), for which the tube diameter expansion is stable around 5.5% already after the second cycle. More than Fig. 9, Fig. 10 illustrates the elastic performance of the new generation of non-woven gauntlets: while the tube diameter of the woven gauntlet (type B) when coming back to 0 bar is 0.3–0.5% higher than its initial value due to the successive dilatations up to 10 bars, the tube diameter of the new generation of non-woven gauntlets is surprisingly smaller than before any tube dilatation (–0.6 to –1.1%). The latter result means that this type of non-woven fabric has improved elastic properties in such a way that the active mass can be even better constrained than in good quality non woven gauntlets during its volume reduction on recharge.

The present study demonstrates clearly that the gap between the woven and the traditional non-woven gauntlets has been filled thanks to the use of flat calendered bicomponent fabrics.

As a result, the use of the new generation of gauntlets might be generalized to any type of filling processes and battery appli-

cations in replacement of woven gauntlets, as the mechanical properties are not a limiting factor anymore.

4. Conclusion

This paper has demonstrated that a wide range of non-woven gauntlets are nowadays available, which could raise the performance of industrial lead-acid batteries, from the standard version with outside tube insulation (well suited for most traction flooded batteries), to the reinforced versions better adapted to more aggressive filling processes.

Especially the new generation of gauntlets (patent pending) made of flat calendered bicomponent fabric combines for the very first time the economical, and electrical advantages of standard non-woven fabrics, with highly optimized mechanical and elastic properties. As a result, the use of the new generation of gauntlets might be generalized to the most demanding filling methods and applications, as the mechanical properties are not a limiting factor anymore. This will enable the battery manufacturer to take advantages of the higher performance and lower price of the non-woven gauntlets in a wider range of battery types, from traction flooded to stationary gel batteries.

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