Technical Update

Recent advances in polyethylene separator technology

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Abstract

The well known technical and production benefits of polyethylene separator materials over other separator materials have prompted a dramatic increase in polyethylene separator usage in recent years. Separator trends in the United States from 1980 to 1996, and in Europe from 1987 to 1992, are shown.

The manufacturing process for polyethylene separators is outlined, with particular emphasis on the latest advances in manufacturing technology. These improvements have resulted in a higher quality product, and also benefit the environment because of the sophisticated oil extraction and solvent recovery system.

The product quality improvements resulting from the latest manufacturing technology include consistent conformance to dimensional specifications, low electrical resistance, close control of residual oil content, virtual elimination of pinholes, and good running properties on the battery manufacturers' plate enveloping machines. The material can also be manufactured with a very thin backweb to reduce electrical resistance still further.

Advantages of polyethylene separators

The technical and production benefits of polyethylene separator materials over other separator materials are now well known and have been the subject of a number of previous papers. These benefits include microporosity, low electrical resistance, high puncture resistance and tear resistance, high oxidation resistance and chemical purity, low acid displacement, flexibility permitting folding without breakage, and ability to be sealed using, e.g., pressweld or ultrasonic weld.

For the battery manufacturer, the ability to envelope the plates has a number of major advantages. These include:

(i) automated plate stacking/battery assembly giving labour savings;
(ii) reduced separator scrap during the assembly process;
(iii) elimination of misaligned or missing separators;
(iv) fewer batteries scrapped in production;
(v) consistent production rates;

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(vi) elimination of shorting caused by side 'mossing' of the positive plate;

(vii) accommodation of grid growth during cycling;

(viii) elimination of battery failures due to separator faults, resulting in a significant reduction in warranty claims.

In addition, when expanded metal grids are used, it is essential that plates be enveloped using polyethylene separator material. The high puncture resistance of polyethylene prevents puncture of the separator material by the sharp edges of the expanded metal grid. Also, the elongation properties of the separator material permit grid growth during cycling without damaging the separator or the seal.

Market background

The above mentioned advantages of polyethylene separators have encouraged a dramatic increase in polyethylene separator usage, particularly in the U.S.A. and Europe, with other countries now also following this trend. This is illustrated in Figs. 1–4. Figure 1 shows separator trends in the U.S.A. from 1980 to 1996. From 1980 to 1986, polymeric separator usage was increasing at the expense of cellulosic. Over the same period glass separators were also increasing in popularity. However, from 1986 onwards, the usage of glass was starting to decline as polyethylene increased its market share, and this trend is expected to continue. Our forecast shows that in 1990, 70% of the market in the U.S.A. will use polyethylene separator materials, and this is expected to rise still further to 90% of the market by 1996. Figure 2 translates this into separator usage in millions of square metres. The forecast growth in polyethylene separator usage in the U.S.A. will result in a requirement for an additional 34 000 000 m^2 of polyethylene separator materials between 1990 and 1996.

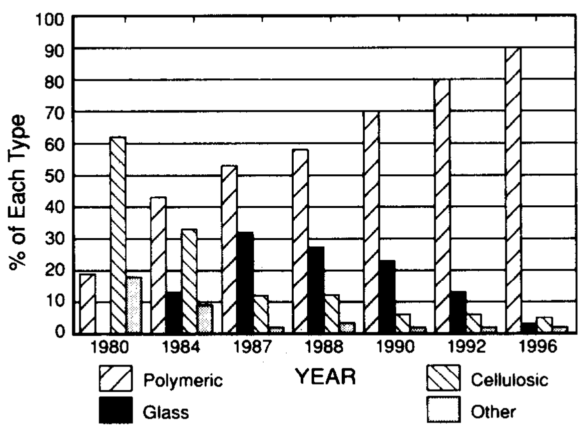

Fig. 1. Separator trends in the U.S.A. Separator type: SLI batteries.

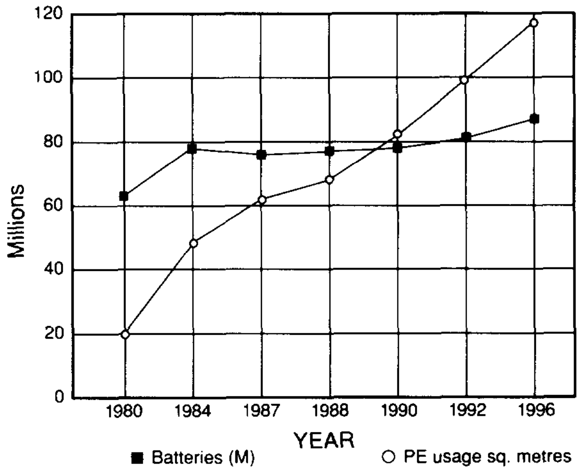

Fig. 2. Polyethylene separator usage in the U.S.A. Square metres: factor 1.5.

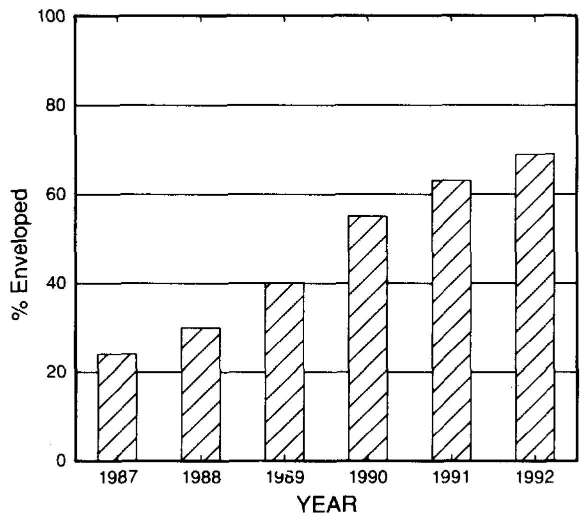

Fig. 3. Separator trends in Europe. Percentage of SLI batteries enveloped.

The leaf-type separator materials used in Europe are mainly cellulosic, with a small proportion of sintered PVC. The glass separator never achieved the market penetration in Europe that it achieved in the U.S.A. because of its high cost. However, the leaf-type separator is now being displaced by polyethylene, as shown in Fig. 3. The latter presents the percentage of SLI batteries that have enveloped separators. Although envelope-separator technology has been slower to gain acceptance in Europe, usage is expected to be 54% in 1990, rising to 70% in 1992. Figure 4 shows projections for polyethylene separator usage, in millions of square metres, through to 1992. This forecasts that between 1989 and 1992 an additional 18 000 000 m^2 of

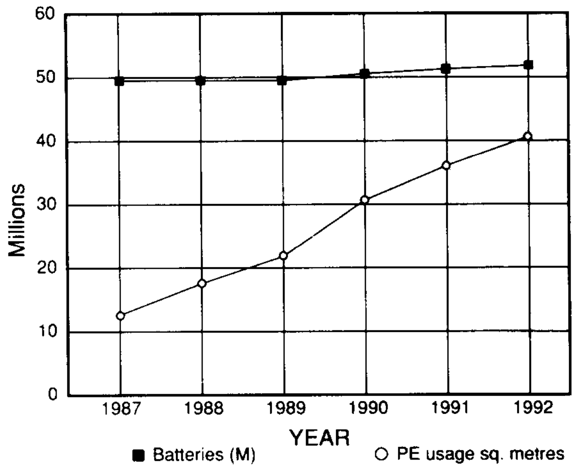

Fig. 4. Polyethylene separator usage in Europe. Square metres: factor 1.12.

envelope separator materials will be needed to satisfy the SLI battery separator requirements.

Our market survey has shown that, in the U.S.A., the average battery uses significantly more separator material than its counterpart in Europe because of differences in the average number of plates per battery. We have therefore used a factor of 1.5 m^2 per battery for the U.S.A., and 1.12 m^2 per battery for Europe.

Because the market for polyethylene separators is less fully developed in Europe than it is in the U.S.A., it is more difficult to forecast the rate of growth of polyethylene separator usage beyond 1992. At present, there is still a significant number of small battery factories (output less than 0.5 million units) that are likely to continue using leaf-type separators for the majority of their production. However, further consolidation in the European battery industry is anticipated. This is likely to result in the closure of the smaller, less economic, battery plants, and the expansion of the more successful ones. The speed of these changes will influence the continuing growth in polyethylene separator usage in Europe after 1992.

Polyethylene separator manufacture

Outline of process

Previous literature concerning polyethylene battery separators has dealt with the market background and the benefits of polyethylene separators, but has not dwelt at any length on the manufacturing technology necessary to produce these separators. We therefore present an outline of polyethylene separator manufacturing technology and show how Entek Manufacturing Inc. has completely redesigned the process.

The basic procedure for preparing polyethylene separator material is the subject of a number of patents. Essentially, it involves blending together polyethylene, silica, and a mineral oil. The latter is subsequently removed using a suitable solvent. The finished separator material contains in excess of 60% silica and, typically, 12% oil. The specification and properties of each of the raw materials are of critical importance to the properties of the finished separator. The properties and specification of the polyethylene and silica in particular have a critical effect on the strength and electrical resistance of the finished product. The polyethylene has an ultra-high molecular weight. The silica is of a purified, precipitated form with a mean particle size less than 1 μm. The silica is essential to the product and remains in the finished sheet. In the manufacturing process, it is the carrier for a liquid, pore-forming agent (normally a mineral oil) which is later removed by a solvent extraction process.

The silica has a highly skeletal structure, prevents the pores from collapsing, is highly absorptive, and naturally acid resistant. Since it is hydrophilic, it imparts wettability to the separator materials and gives rise to a low electrical resistance. The processing oil — which is removed in the solvent extraction process — acts as a plasticiser during the extrusion process. Some of the oil (normally 9–15%) remains in the finished product to impart flexibility to the separator.

The Entek manufacturing process

The Entek manufacturing operation is a continuous process from the mixing of raw materials through to slitting of the finished product. Together with the other process improvements detailed below, this results in a very compact manufacturing plant (Fig. 5).

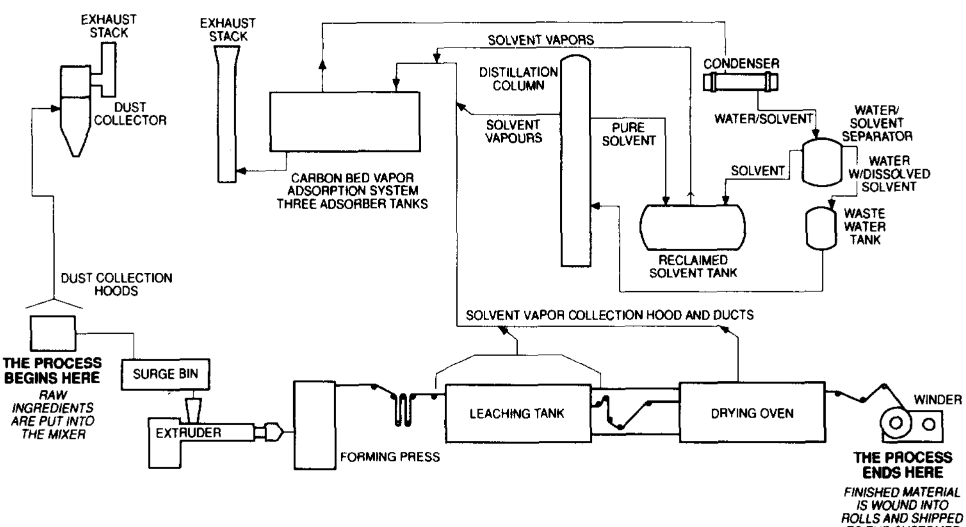

Fig. 5. Entek's process for manufacturing microporous membrane.

One of the major problems with processing a highly filled polymeric sheet is the degree of shrinkage that can occur during the process. If this shrinkage is not controlled, the dimensions of the finished sheet will not meet the specified values. Entek has reduced this problem by using a narrower line width of about 730 mm (29 in.), approximately half that used by other polyethylene separator manufacturers. This means that a lower roll camber is required, enabling closer control over thickness and width. Width shrinkage during the oil extraction process is less of a problem. Coupled with the close control of the operating parameters, this enables the sheet width to be controlled within very close tolerances.

With the Entek line design, thinner backwebs are achievable, while maintaining an acceptable strength. Backwebs of 0.125 mm are already being produced–half the current normal backweb.

Mixing/blending/extrusion processes

By improving the mixing and extrusion processes, Entek is able to use a higher molecular weight polyethylene to impart a higher strength to the finished product. The special extruder screw design provides extensive mixing and shear, and facilitates the breakdown of large raw material particles. This provides a small, uniform pore size, together with a narrow pore-size distribution. The result is that the finished product has a very low electrical resistance. The properties of the silica (i.e., particle size, pH, etc.) must be carefully specified, as these also affect the electrical resistance of the finished product.

Calendering process

The blended thermoplastic material passes directly from the extruder to the patented calendering process in which the desired thickness is achieved, and the rib pattern is imparted to the sheet material. The sheet passes between a pair of heated calendering rolls and then over a cooling roll. The middle roll has the separator profile cut into it.

The allowable temperature range for the calendering process is very narrow. If the temperature of the rolls is too high, the material sticks to the rolls, and if the surface temperature is too low, the sheet is too brittle. In a conventional calendering process, it is very difficult to control the temperature within such close limits. This is a particular problem with the highly filled, ultra-high molecular weight polyethylene compositions that are used for the manufacture of polyethylene separators as described in this paper.

Entek has developed a patented method to overcome this problem by the design of the calender rolls and the use of wet steam (saturated) to heat the rolls. The wet steam is introduced into cavities in the rolls, and is maintained at a constant pressure to ensure that the outer surfaces of the rolls are held at a constant temperature, irrespective of the temperature of the sheet or of ambient temperature. The equilibrium between the water and steam at a given pressure ensures that the outer surfaces of the rolls are maintained at the correct temperature to prevent sticking, and to give a uniform sheet gauge.

The calendering process also results in a finished product which has extremely good elongation and strength characteristics.

Oil extraction process

The patented oil extraction and solvent recovery system is an important feature of the Entek process. It is designed to ensure that the solvent used does not escape either into the workplace or to the atmosphere outside the plant.

The solvent used to extract the oil is trichloroethylene, a non-flammable chlorinated hydrocarbon. Solvent emissions to the atmosphere are strictly controlled. In the U.S.A., the maximum allowable workplace concentration is 50 ppm. Allowable atmospheric emission varies from State to State, but in Oregon it is controlled as a volatile organic compound (VOC) at a maximum of 10 ppm. At present, there is no legislation in Europe controlling maximum emissions of trichloroethylene, but it is anticipated that legislation will be introduced in the near future.

The oil extraction tank itself is only 3 m long, compared with around 100 m in other systems. The sheet material passes over a series of rollers at the top and bottom of the tank to increase the contact area of the sheet with the solvent. The solvent is heated so that it is vaporised to form a cleaning zone containing the vaporised solvent above the liquid zone. At the top of the tank, the solvent is condensed and returned to the bottom of the tank. As the sheet passes through the tank, it is in contact both with the vaporised solvent, and with the liquid solvent as it condenses and collects at the bottom of the tank. This compact extraction process reduces the oil content from 65% to 12% and the final oil content can be very closely controlled. The solvent used is continually recovered and returned to the process and the oil removed from the sheet is also recovered and is re-used to make additional separator material.

Since the solvent remains in a closed system, there is no loss to the environment. This minimises the cost of replacing solvent and prevents pollution. Also, any trichloroethylene vapour that might escape from the process is captured and fed to a sophisticated solvent recovery plant (Fig. 5). This ensures that trichloroethylene release to the atmosphere is consistently below 5 ppm.

When the separator sheet emerges from the oil extraction tank, it passes to a solvent extractor in which steam is directed onto the sheet to displace the solvent in it. The final stage is to remove steam from the pores of the sheet material by passing it through a drying oven.

Control of the percentage of oil in the finished product is very important as it affects the electrical resistance of the separator. If the oil content is too high, some of the pores will be blocked, resulting in a higher electrical resistance. If the oil content is too low, this will adversely affect the flexibility and elongation of the separator. The Entek oil extraction process enables the oil content in the finished sheet to be maintained within very close limits.

Pinhole detection

The finished product must be essentially free from pinholes, and any that do occur must be marked with a coloured dye so that the battery manufacturer can remove the offending material during the assembly process. The standard specification permits a maximum of 15 pinholes per 1000 m length. Separator suppliers are under pressure from battery manufacturers to tighten this specification. As speeds of enveloping machines increase it becomes less and less desirable to stop the machine to remove faulty material.

With the Entek manufacturing line the finished sheet is continuously monitored for pinholes as it passes out of the drying oven and before it is slit. A high intensity light shines through the sheet and this is monitored by a camera placed above the sheet. Any pinholes that are detected are automatically sprayed with a dye and the number of pinholes per sheet is automatically counted. This system is extremely sensitive, and it is possible to detect pinholes as small as 2 μm. In other words, this system will detect pinholes that are smaller than the average pore size of a cellulosic-based, leaf-type separator! In practice, because the entire process is so carefully controlled, the majority of the rolls of separator material produced have no pinholes at all, and all the material produced is within the specification.

Slitting/coiling

The final stage of the process is the slitting/coiling operation. The edge of the sheet is continuously monitored and adjustments made to ensure that the material coils up smoothly. The tension is also closely controlled to ensure that the battery manufacturer does not experience any problems when the sheet is unwound.

Process control

As part of the sophisticated manufacturing technology, a control computer is used to monitor the process operating parameters and the data are recorded for subsequent analysis. The continuous monitoring of the process ensures that dimensional accuracy, oil content, etc., are maintained exactly on specification. All the relevant operating data are stored and can be recalled later to assess trends, evaluate causes of substandard material, etc. The use of statistical process-control techniques provides valuable information, both for the separator supplier and for the battery manufacturer who uses the material. A capability report provided to the battery manufacturer furnishes the necessary assurance of quality.

A separate computer controls the environmental equipment that removes trichloroethylene from the exhaust air. This computer also controls the bulk storage tanks.

Product quality improvements

The process improvements outlined above supply the battery manufacturer with the following quantifiable product improvements.

Consistent product quality

In order to maintain a high productivity through the plate enveloping machine, the battery manufacturer must receive separator material that is consistent in its dimensional properties. The practical term often used to describe this is 'runnability'. Of particular importance is the 'shoulder' dimension, i.e., the distance between the last main rib and the edge of the separator. It is in this shoulder area that the sealing takes place, and normally there are 'mini-ribs' to assist the sealing process.

Control of the overall thickness is important as this may affect the ease with which the cell group fits into the battery container. If the separator material consistently has an overall thickness that is close to the maximum, or minimum, allowable thickness, this may cause problems even if the material is within specification, as the battery design will have been based on an average value for the separator thickness.

The separator backweb also needs to be closely controlled to ensure that the separator has a consistently low electrical resistance.

Process control and monitoring with the Entek process ensure that all these dimensions are kept as close as possible to the mean value of the specification. Sheet width and thickness are continuously monitored by the production operators and recorded for each roll produced. This is in addition to the quality control data for each roll. The latter are recorded by the quality control laboratory.

Lower electrical resistance for given backweb thickness

The electrical resistance of the separator is one of the critical factors affecting the cold cranking performance of an SLI battery. A low electrical resistance is one of the inherent properties of a polyethylene separator because of its microporosity combined with a high, overall porosity and a thinner backweb than cellulosic materials. With the Entek process, the electrical properties of the separator are further improved by altering the raw materials' formulation to include a higher proportion of silica. This is made possible because Entek's mixing and extrusion processes enable an ultra-high molecular weight polyethylene to be used. This results in a separator material with a very low electrical resistance and high overall porosity.

Thinner backweb materials

Since there is a direct relationship between the backweb thickness and the electrical resistance, an obvious way to reduce electrical resistance further is to reduce the backweb thickness. However, the integrity and strength of the material must be retained, with no increase in the number of pinholes. With the Entek technology it is already possible to reduce the backweb thickness to 0.125 mm (0.005 in.) while maintaining the strength, puncture resistance, and overall product quality. Selected battery manufacturers now have this material undergoing production trials. Some modification to the plate enveloping machinery may be needed to run this thinner material. The thinner material has the main ribs much closer together to improve the strength and 'runnability' of the material.

This thin backweb material is not being used in routine production yet by any of the battery manufacturers. However at least one battery manufacturer in the U.S.A. is already successfully using material with a backweb of 0.165 mm (0.0065 in.).

Figure 6 shows the relationship between backweb thickness and electrical resistance for separator backwebs in the range 0.125–0.46 mm.

Residual oil content

At the start of the separator manufacturing process the sheet material contains about 65% oil; this is adsorbed on the silica. It is the removal of this oil during the solvent extraction process that creates the microporosity in the finished separator material. However, it is desirable to retain a certain amount of oil in the finished product so that the separator has the required properties of flexibility and high strength. The normal specification is $12 \pm 3\%$ oil in the separator.

Users of industrial batteries with automatic topping-up systems have noticed that, under certain operating conditions, the valves used in the topping-up devices can become blocked. This has been attributed to the oil in the separator leaching out into the acid.

With the Entek process, the final oil content is closely controlled to the exact level required, and it is not necessary to add any additional oil at the end of the extraction process. It is believed that the oil, which is intimately mixed with the silica during the mixing and blending process, is less likely

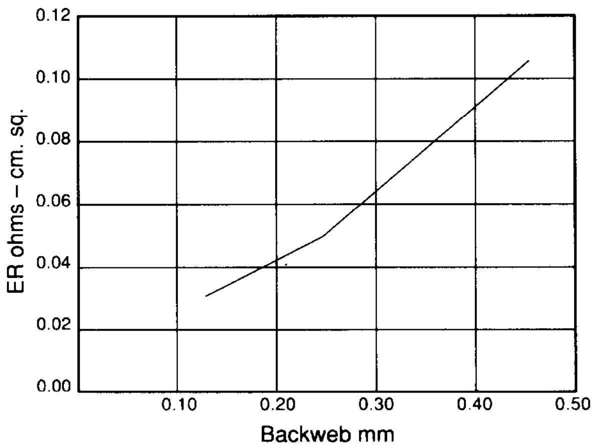

Fig. 6. Backweb vs. electrical resistance. Entek polyethylene separator.

to be leached out of the separator than the oil which has to be re-added after the extraction process (as may be the case with other manufacturing processes).

It may also be possible to reduce the oil-release problem with industrial separators by producing material with a lower final oil content, while maintaining satisfactory separator properties.

There is still some dispute concerning the exact reason for the valves in certain automatic topping-up systems becoming blocked when polyethylene separators are used, and there is some evidence that the problem may be worse if the separator contains a voltage-control additive. Obviously, this is an area where further work is needed, particularly for the industrial battery market.

Freedom from wavy edges/camber

If the polyethylene has significant wavy edges or camber, this will affect the ease with which it will run through the enveloping equipment, and productivity may be seriously affected. The narrow line-width of the Entek plant reduces this problem. The control features at the slitter also ensure good edge and tension control.

Elimination of pinholes

A pinhole (or other defect such as a tear in the separator material) may cause premature battery failure in service if it permits a short-circuit to occur between plates of opposite polarity. This is a failure mechanism which is almost impossible to detect by the usual high-rate discharge test at the end of the assembly line, as it will not normally become apparent until the battery has been in service for some time. The separator manufacturer must therefore ensure that any pinholes, or other defects in the product, are detected and marked. Since the separator material is supplied on a continuous roll, it has become acceptable practice for the area in the vicinity of the pinhole to be sprayed with a dye. This enables the defect to be picked up by the battery manufacturer when the separator material is run through the plate enveloping machine.

It is not satisfactory to rely on a manual system of pinhole detection, as this then becomes a somewhat 'hit-and-miss' affair, dependent on the skill and interest of the operator. Entek therefore uses an automatic system of pinhole detection, as described earlier. This has the added benefit that smaller pinholes can be detected than would be the case with a manual detection system.

Future developments

Manufacturers of battery separators are constantly researching new and improved materials. This technical note has sought to show that the Entek manufacturing technology will enable the polyethylene battery separator material to stay ahead of rival materials for many years to come. The high quality, toughness, low electrical resistance, and low manufacturing costs of the Entek polyethylene separator material set standards that other materials will find hard to match. The ability to manufacture the separator material with very thin backwebs should be of particular interest to battery manufacturers wishing to develop new battery designs with even higher cold-cranking performance. However, the battery industry never stands still and, for example, there may emerge a future trend towards the sealed gas–recombinant lead–acid battery for SLI applications. Entek is already developing new or improved separator materials to meet the needs of tomorrow's batteries. Another Cookson Group Company – Scimat – manufactures very thin microporous membranes for other types of batteries including lithium batteries. Joint development work between Cookson Entek and Scimat will undoubtedly result in further advances in battery separator technology.