



Manufacturing Processes of Microporous Polyolefin Separators for Lithium-Ion Batteries and Correlations between Mechanical and Physical Properties

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Abstract: Rechargeable lithium-ion batteries (LIBs) have emerged as a key technology to meet the demand for electric vehicles, energy storage systems, and portable electronics. In LIBs, a permeable porous membrane (separator) is an essential component located between positive and negative electrodes to prevent physical contact between the two electrodes and transfer lithium ions. Among several types, microporous polyolefin membranes have dominated the commercial separator market for LIBs operated with liquid electrolytes, favored for their chemical and electrochemical stability, high mechanical strength, uniform pore size, and inexpensive manufacturing and materials cost. In this review, we summarize the principles and theoretical background underlying conventional manufacturing processes and newly emerging microporous polyolefin separators. Based on their mechanical and physical properties, as collected from the literature, we introduce a number of processing type-dependent characteristics and universal correlations among their properties. This will provide a macroscopic view on the subject and a guideline for the development of next-generation separators.

Keywords: separators; lithium-ion batteries; mechanical properties; polyolefin

1. Introduction

With the rapidly growing demand for power consumption, lithium-ion batteries (LIBs) have emerged as a sustainable energy source for portable electronic devices and energy storage systems owing to their high specific energy and power (Figure 1a), flexible and lightweight design, and long lifespan compared with other battery technologies [1]. LIBs operate at voltages >4 V via reactions involving lithium ions at electrodes during charge and discharge. The following are examples of the reactions occurring in the operation of LIBs with LiCoO₂ and graphite as a cathode and anode, respectively, as described in Figure 1b [2]:

Cathode:
$$LiCoO_2 \leftrightarrow Li_nCoO_2 + nLi^+ + ne^-$$
 (1)

Anode:
$$6C + nLi^+ + ne^- \leftrightarrow Li_nC_6$$
 (2)

A separator is a porous permeable membrane that can transport Li⁺ ions formed or consumed by the aforementioned reactions. In various types of commercial LIBs, the main function of the separator is to prevent short circuits caused by physical contact of the two electrodes (Figure 2) [3]. Thus, the chemical and electrochemical resistance of the separator as well as its mechanical durability are critical to battery safety. The separator should not be dissolved by or react with the electrolyte solution, which is mainly composed of organic carbonates and esters mixed with Li salts, such as lithium hexafluorophosphate [4]. In addition, it must be electrochemically stable during cell operation and mechanically strong enough to withstand the high tension in the course of battery assembly [5]. The mechanical strength is also required to avoid cell short circuiting and thermal runaway via the penetration of lithium dendrites through the separator as a result of the plating of



Citation: Mun, S.C.; Won, J.H. Manufacturing Processes of Microporous Polyolefin Separators for Lithium-Ion Batteries and Correlations between Mechanical and Physical Properties. *Crystals* **2021**, *11*, 1013. https://doi.org/10.3390/ cryst11091013

Academic Editors: Jiehua Liu, Fancheng Meng and Yi Sun

Received: 30 June 2021 Accepted: 22 August 2021 Published: 24 August 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). metallic lithium on the surface of graphite anode during cycling [6]. The microstructure of the separator should be carefully designed. A separator with large pores is more susceptible to shorts and self-discharge, especially during high-temperature storage, as well as failure during the high-potential (hi-pot) testing. At the same time, a small pore size can lead to higher resistance and poor cycle life during high-temperature cycling and storage [7]. Higher porosity is also preferable as more liquid electrolyte can be stored to achieve higher ionic conductivity, but it will also result in mechanical properties inferior to those of less porous separators.







Figure 2. Schematics of inner structures of commercial LIBs. (**a**) Cylindrical-type, (**b**) prismatic-type, and (**c**) pouch-type cells. Reproduced with permission from [3].

Separators are typically classified into six types: microporous membranes, nonwoven membranes, electrospun membranes, membranes with external surface modification, composite membranes, and polymer blends [8]. Despite the poor thermal stability and wettability of liquid electrolytes, the microporous membranes have dominated the overall market in the LIB industry based on low cost and simplicity of fabrication over other types. In particular, those with ceramic coating have been regarded as the best currently available option. The advantages and disadvantages of each type of separator are documented in a comprehensive review [8].

As base films for such safety-enhanced ceramic-coated separators, microporous polyolefin membranes have the merits of high porosity and uniform pore-size distribution, electrochemical stability at 4.2 V or higher vs. Li⁺/Li [9,10], high mechanical strength, and inexpensive materials and manufacturing. In recent years, commercial microporous polyolefin separators have been made thinner, decreasing to <20 μ m, as a means of maximizing the energy density of portable electronics and electric vehicles. However, this lowers the maximum endurable mechanical load and dimensional stability at elevated temperatures, thereby making the assembled battery more vulnerable to external damage. The risks associated with thin separators have been demonstrated by thermal ramp tests, overcharge tests, and induced internal and external short circuit tests [11]. In addition, a larger mean pore size and higher porosity generally result in lower ionic resistance and thus high specific battery power [12]. In this case, the poorer mechanical strength is expected to increase the possibility of inner-battery electrical short circuiting. It is thus necessary to compensate for the side effects the separators may encounter and to preserve their safety.

The present review will focus on microporous polyolefin separators for LIBs working based on liquid electrolytes. We will introduce both conventional and new manufacturing processes for commercial separators based on the underlying physics and associated theory. This review aims to compare the mechanical and physical properties of different types of separators and understand the correlations between them. This may allow for the proper design of next-generation separators and the tailoring of their mechanical and physical properties.

2. Manufacturing: Dry and Wet Processes with Uniaxial or Biaxial Stretching

2.1. Dry Processing for Microporous Polypropylene Separators

In industry, uniaxially stretched dry-processed polypropylene (PP) membranes and biaxially stretched wet-processed polyethylene (PE) membranes have been major focuses of manufacturing. The typical surface morphologies of these membranes are presented in Figure 3. In the dry process with uniaxial stretching, polyolefin melt is extruded and cast or blown into a film and annealed at a temperature between the glass transition temperature and the melting temperature (T_m) to increase crystallinity and control the size of crystallites. Then, the melt is stretched in the machine direction (MD). In this process, a row lamellar crystal structure is generated, and the lamellar interfaces are subsequently torn to form highly oriented slit-like micropores in the course of uniaxial stretching (Figure 3a) [13,14]. The anisotropy of dry-processed uniaxially stretched PP membrane leads to a significant imbalance in tensile strength between the MD and the transverse direction (TD) along with poor tear strength, whereas the tensile strengths of wet-processed separators are comparable between the two directions, which will be discussed in Section 4. Kalnaus et al. explain this imbalance according to the higher tensile strength of fibrils than nodes, since the fibrils are pre-deformed and hardened by the orienting of polymer chains (strain hardening) during the course of stretching [15]. To overcome this disadvantage of uniaxially stretched dry-processed PP separators, special techniques have been developed with the aim of applying biaxial stretching to PP via a dry process.



Figure 3. SEM micrographs of microporous polyolefin membranes at the surfaces. (a) Uniaxially stretched dry-processed PP separator. (b) Biaxially stretched dry-processed β -nucleated PP separator. (c) Biaxially stretched wet-processed PE separator. (scale bar = 5 μ m) Reproduced with permission from [14].

Although the uniaxial stretching technique has dominated the dry-processed PP separator market, the dry biaxial stretching of β -nucleated isotactic PP has also been employed to produce microporous membranes [16–19]. The metastable β phase does not appear in the phase diagram [20], and it must be generated under special crystallization conditions or in the presence of an efficient β -nucleating agent [17,18,21]. β -nucleated PP

is known to have higher tensile and fracture toughness than isotactic PP with α -crystals owing to the β - α polymorphic transition induced by mechanical stress [22,23], which is also the mechanism of pore formation in β -nucleated PP. Unlike the uniaxial stretching of α -crystalline PP film, microvoiding occurs via volume contraction by the transition of β crystals to the more stable α form or bulk volume shrinkage in the presence of stable β crystals [16,19]. The creation of micropores can be initiated from the weak interfaces between β -lamellae [17]. Dry biaxial stretching can also balance the tensile strength between the MD and the TD, as represented by the resulting morphology (Figure 3b), making it more economical than the wet process with biaxial stretching. However, biaxially stretched dry PP membranes have large pore sizes and broad pore distributions, which may limit their application [17]. Another approach has been reported for the dry biaxial stretching of PP films for battery separators in which there is no implication of β -nucleation. In this case, the extruded PP cast film is biaxially stretched in both the MD and the TD. It should be noted that the stretching process in the TD includes a simultaneous controlled relaxation of the films along the MD [24]. The pore morphology of the resulting membrane included a round shape and a low aspect ratio around 1, clearly differentiating it from both β-nucleated biaxially stretched PP separators and uniaxially stretched PP separators. This process also balances the tensile strength between the MD and the TD while possessing the benefits of dry processing. The mechanical and physical properties of these biaxially stretched PP separators will be discussed in comparison with other separator types in Sections 4 and 5.

2.2. Wet Process for Microporous Polyethylene Separators

In wet or phase-inversion processes, thermally induced phase separation is a major mechanism in the formation of micropores. In a typical wet process with biaxial stretching, hydrocarbon liquid (or low-molecular-weight diluent) is mixed with polyolefin above its T_m , extruded into a casting film, and then stretched in both the MD and the TD, as depicted in Figure 4 [14]. Micropores are then formed after extracting the hydrocarbon liquid with a volatile solvent. Paraffin oil and methylene chloride are the most commonly used hydrocarbon liquid and solvent, respectively, for PE membrane [5]. Although the phase separation of the mixture containing PP and diluents is plausible [25], the wet biaxial stretching of PP has rarely been reported for battery separators. Distinct from the dry process, the extraction here is an essential step and it is the main cause of the increase in manufacturing costs. In addition, a heat-setting process enhances the dimensional stability and prevents shrinkage or wrinkle formation upon heating, which is important for safety and control of the final performance [26,27]. The phase separation type varies with the components and processing conditions. For example, solid–liquid (S–L) phase separation has been observed in the processing of ultrahigh-molecular-weight PE (UHMWPE)-liquid paraffin (LP) blends, although they exhibit upper critical solution temperature (UCST)type phase behavior [28]. In contrast, liquid–liquid (L–L) phase separation has also been observed in UHMWPE–LP blends at different quenching temperatures [29]. It should be noted that S-L separation is usually initiated by crystallization [28], whereas L-L separation is instead induced by the thermodynamic instability of the blend system [30]. The phase separation process significantly affects the final morphology of the membrane. For example, the cooling rate in S–L separation is known as a major determinant of pore size and mechanical properties, whereas the time period in the L-L region has the greatest influence on the morphology of a membrane formed via L–L separation [30]. The main advantage of PE separators is their high and well-balanced mechanical strength in both directions, as reflected in their less anisotropic pore structure (Figure 3c) compared with uniaxially stretched PP (Figure 3a).



Figure 4. Schematic of typical PE separator wet manufacturing process with biaxial stretching. Reproduced with permission from [31].

2.3. Biaxial Stretching of Separators: Simultaneous and Sequential Stretching

The biaxial stretching of PP or PE separator films may be achieved either simultaneously or sequentially. In sequential biaxial stretching, the cast film is stretched along the MD while increasing the speed between rolls. A tenter frame stretches the entering film in the TD, while the film is gripped along each side by clamps attached to moving chains and passes through heated zones in an oven [27]. Simultaneous biaxial stretching is available for both the blowing process and tenter frame (Figure 5). In this case, the cast or blown film is stretched along both directions (MD and TD) at the same time in a single process. In simultaneous stretching by film blowing (the double-bubble method), the thick-walled tube-like melt is extruded from a circular die and blown under air pressure to orient the film in the TD, while MD orientation is achieved by adjusting the speed at which the tube is pulled downwards and collapsed [27]. Simultaneous stretching with a tenter frame can prevent scratches and the introduction of contaminants on the surface of the cast film caused by contact with the rolls during MD stretching, while these may be present in sequential stretching [32]. At the same time, sequential stretching with a tenter frame is advantageous in terms of its high production speed, wide-film production capability, low equipment cost, and relatively uniform resulting film thickness. However, it suffers from smaller processing temperature windows and draw ratios [33] than does simultaneous stretching. To improve the productivity and quality of films, continuing efforts are being made to devise new types of simultaneous biaxial stretching equipment [32,33].



Biaxial orientation technologies

Figure 5. Schematics of sequential and simultaneous biaxial stretching processes. Reproduced with permission from [33].

3. Thermal Stability for Safety Features

From the perspective of the safety of LIBs based on their crystalline melting behavior, PE and PP membranes each have their own advantages. The T_m of PE and isotactic PP are approximately 135 °C and 165 °C, respectively. Microporous polyolefin separators also have important features based on their thermal properties, namely, shutdown, meltdown, and thermal shrinkage. Shutdown is a function of increasing resistance based on the self-blocking of micropores (Li⁺ ion pathways) in the case of abnormal temperature rise, which leads to a shut-off of battery reaction to prevent further increases in temperature [34]. If shutdown occurs at unusually low temperatures, the LIB will be inactivated from normal operation. On the other hand, thermal runaway cannot be prevented or delayed by shutdown if it occurs at very high temperatures. LIBs have been designed such that thermal shutdown begins at a temperature around 130 °C or 160 °C when using PE or PP as the separator, respectively [35]. It is important to note that these temperatures at shutdown are close to the T_m [36]. If the heat generated is much greater than the heat dissipated, the whole separator may melt completely (i.e., meltdown), such that the electrodes come into contact with each other directly, leading to a short circuit [35].

Meltdown is not the only cause of short circuiting, as thermal shrinkage is also common in stretched PE [37] and PP films [38]. When a stretched film is subjected to a sudden increase in temperature, it shrinks as a result of the relaxation of polymer chains that were oriented under stress [39]. For this reason, uniaxially stretched PP membranes shrink only a small amount in the TD. Thermal shrinkage can be alleviated by a heat-setting process accompanied by a moderate change in pore size, porosity, ionic conductivity, and so forth [26]. It is of great interest to increase the meltdown temperature as much as possible or minimize the thermal shrinkage while maintaining a reasonably low shutdown temperature. This can be achieved by coating functional layers with ceramic particles [40-42] or a polymer with high thermal stability [36,43] on the polyolefin separators. Figure 6 shows the improvements in meltdown temperature and thermal shrinkage of pristine PE via coating with Al₂O₃ particles using poly(vinylidene fluoride-co-hexafluoropropylene) as a polymeric binder [44]. As shown in Figure 6a, thermomechanical analysis (TMA) in tension mode is an informative method for monitoring dimensional change (thermal shrinkage and expansion) based on the ramping of temperature to identify the meltdown temperature of a separator. In addition, thermal shrinkage is commonly measured by change in lateral size after a certain period of isothermal treatment (Figure 6b).



Figure 6. (a) TMA thermograms and (b) thermal shrinkage of pristine PE and Al₂O₃-coated PE separators. Reproduced with permission from [44].

Multilayered structures have also been proposed to integrate the advantages of PE (low shutdown temperature at ~130 °C) and PP (high meltdown temperature at ~165 °C) into polyolefin separators, even without functional coatings. For example, PE–PP bilayer and PP–PE–PP trilayer structures have been commercialized by separator manufacturers. The morphology of a PP–PE–PP trilayer separator is presented in Figure 7. Multilayered

membranes can be manufactured using a lamination process, a coextrusion process, or a combination of the two [45]. The PE layer increases the resistance of the electrolyte filled inside the membrane at temperatures lower than the thermal runaway temperature, whereas the PP layer maintains its mechanical integrity to prevent a short circuit between the electrodes. However, considering the technical difficulties in and complexity of multilayer film fabrication processes, it would be useful to devise a simple and economical manufacturing process to achieve a low shutdown temperature and high meltdown temperature in a single-layered membrane.



Figure 7. (a) Surface and (b) cross-sectional scanning electron micrographs of a PP–PE–PP trilayer separator (Celgard 2325). Reproduced with permission from [13].

4. Mechanical Properties

The mechanical properties of separators are of particular interest as measures of their durability during battery manufacturing and cell cycling. The main parameters of concern are the tensile strength along the MD and TD, the tensile elastic modulus, and the puncture strength, although these do not provide a full understanding of the mechanical behavior [15,46]. For instance, these properties can be indicative of the integrity of separators with regard to withstanding tension from winding machines [15] or cutting of the separator during cell assembly, whereas they are poor at predicting the compressive stack pressure a separator may experience during battery aging [47]. Despite this limitation, tensile properties and puncture strength have been widely adopted owing to the simplicity of the associated measurements. The ultimate tensile strengths of unmodified non-porous highdensity PE (HDPE) and PP are typically around 3.0 and 3.3 MPa (310 and 340 kgf/cm²), respectively, with elongation at break up to 600% and 400%, respectively [48]. With uniaxial or biaxial stretching, their tensile strength in the drawn direction(s) increases readily up to >1000 kgf/cm². Molecular weight [49,50], draw ratio [34,49,51], drawing temperature [50], thermal annealing [51-54], and heat setting [26] are common factors used to control the porosity and pore size, film thickness, crystalline structure, and orientation of micropores and crystals, thereby affecting the final mechanical properties. In addition, incorporating UHMWPE in wet-processed PE separators improves both their tensile strength and puncture resistance [34]. However, a HDPE–UHMWPE–LP mixture with high viscosity may limit processibility given a high UHMWPE content.

The tensile strengths of microporous polyolefin membranes in the MD and TD are shown in Figure 8a. Because most single- or multilayered PP-based separators are manufactured by dry uniaxial stretching, the tensile strength in the TD is much lower (<250 kgf/cm²) than that in the MD, owing to the high anisotropy of the microstructure. In contrast, biaxially stretched PP separators possess moderate tensile strength in the TD (300–1000 kgf/cm²). However, their tensile strength should be improved to compete with commercial PE separators. In most PE separators, the tensile strength in the MD and TD are relatively well balanced and tend to be over 1000 kgf/cm².

Puncture strength is another parameter frequently used in membrane evaluation. It is believed that a high puncture strength is required to prevent internal micro-short circuits

caused by the growth of Li dendrites through the separator or by foreign materials, such as small metallic debris, in lithium-based batteries [55,56]. Typical reported puncture strength values range from 200 to 600 gf. The puncture strength is not correlated with tensile strength in any direction because it depends on the membrane thickness. Instead, the tensile strength in the MD has a greater correlation with the puncture strength per thickness.

The positive relationship between the two parameters is shown in Figure 8b. It is worth noting that wet-processed PE-based separators are more puncture resistant than dry-processed PP-based separators, as can be seen based on the example of a UHMWPE separator (denoted as P-class) and PP-PE-PP trilayer separator (Celgard 2325) [57] used in a previous study (Figure 8c). After puncture fracture tests, Celgard 2325 was split along the MD by a line-shaped hole, whereas the mode of failure in the UHMWPE membrane was localized around the pinhole [57] (Figure 8c, inset). The inferior puncture characteristics of PP-based separators may be due partially to their unbalanced tensile strength and weak tear resistance based on a highly aligned microstructure. However, this assumption does not explain the low puncture strength per unit thickness of biaxially stretched dry-processed PP separators (Figure 8b), which do not exhibit significant orientation in a particular direction or unbalanced physical properties between directions. In addition, when PP and HDPE were uniaxially stretched by dry processing with the same draw ratio in a previous study, the puncture strength per thickness of PP (14 kgf/ μ m) was considerably higher than that of HDPE (8 kgf/ μ m) [58]. Thus, it is more reasonable to assume that this distinction originates from the different fibril structures formed by wet and dry processing, i.e., more developed tortuous pathway beneficial for resistance to puncture.



Figure 8. Correlations among mechanical properties of microporous polyolefin separators. (**a**) Tensile strength in the MD and TD [5,14,24,45,59–64]. (**b**) Puncture strength per thickness plotted against tensile strength in the MD [14,45,59–62]. (**c**) Examples of force–penetration displacement curves of P-class (UHMWPE separator) and Celgard 2325 (PP–PE–PP trilayer separator) for puncture resistance test. The inserts are the images of the samples after puncture fracturing. Reproduced with permission from [57].

5. Porosity and Air Permeability

Besides the aforementioned mechanical considerations, various physical parameters are closely related to the lithium-ion conduction of separators. In particular, porosity, pore size, electrolyte absorption and retention, and air permeability are the physical characteristics or parameters of primary concern [8]. Some of these factors are also highly interrelated. One example is the correlation between porosity and air permeability. Porosity is an important physical parameter of LIB separators. The typical porosity of microporous polyolefin separators is 35–55% (Figure 9a). Interconnected micropores with greater volume facilitate lithium ion transport by retaining more liquid electrolytes. However, it is a complicated issue to judge whether high porosity is beneficial for battery performance. In previous research, with the same thicknesses, separators with lower porosity resulted in higher specific capacity than with higher porosity [65]. However, the separators were manufactured

with different materials and processing types, which will differ in structural characteristics. Hence, as discussed in another report, tortuosity should be taken into account along with porosity and thickness [66]. In fact, a very high porosity may have an adverse impact on battery safety owing to low mechanical strength and high shrinkage caused by increases in temperature [67] or weak resistance to lithium dendrite growth. Within a practical porosity range (35–55%), there is no overall tendency toward decreasing tensile strength (in the MD) as porosity increases (Figure 9b).

Air permeation is indicative of ionic conductivity because of their connection through the phenomena of fluids passing through porous media. It is believed that they will be proportional to each other in an ideal case, such as in the perfect wetting of a separator by electrolyte solution. The Gurley value (measured in seconds) is a simple and effective measure of air permeation through a separator. The Japanese Industry Standard defines the Gurley value as the number of seconds required for 100 cm³ (100 mL) of air to pass through 2.54 cm² of a given material at a pressure difference of 12.40 cm of water (1.21 kPa) [46]. Its units are seconds or s/100 mL, both of which are distinct from the conventional units used for air permeation (i.e., mol/sm^2Pa). However, the inverse of Gurley seconds can be interpreted as the air permeation with fixed measurement conditions (pressure difference and area) that are not explicit in the units. This must be differentiated from air permeability, which is an intrinsic property independent of thickness as well as pressure difference. Instead, the inverse of Gurley seconds per unit thickness (Gurley/thickness) is equivalent to air permeability. In theoretical and experimental work on fluid flow in various porous media, the discovery of a functional correlation between the permeability and macroscopic properties of a medium has been attempted [68]. Among such properties, the porosity (Φ), specific surface area (S), and tortuosity (τ) have been adopted to account for the permeability of flow (k). This relationship can be explained by the Kozeny-Carman equation, as expressed below [68,69]:



Figure 9. Correlation between porosity and (**a**) the Gurley/thickness (log-log plot) [5,13,14,45,59–61,70–73] and (**b**) tensile strength in the MD of microporous polyolefin separators [5,14,24,45,59,61,63,64].

Here, c is the Kozeny coefficient, which depends on the geometry. Neglecting the dependency of S and τ on the porosity, the Gurley/thickness is inversely proportional to Φ^3 . Experimental results reported in the literature have demonstrated that the slope of a fitted line of log(Gurley/thickness) and log Φ is -3.2, which is close to the estimated value of -3 (Figure 9a).

In addition, one can draw an analogy between air permeation (Gurley value) and electrolyte resistance (ER), in that the fluids pass through a microporous media. Air permeability is indicative of both porosity and tortuosity [13]. However, this relationship was not investigated in the present review because of a lack of reported ER values for base separator films and the discrepancy in ER caused by the composition of liquid electrolytes and Li salt concentrations. Apart from this, there are more universal and type-dependent correlations between physical parameters of microporous polyolefin separators. These were not investigated in this review but are well documented in other reviews and research papers.

6. Summary and Outlook

With increasing demands for energy density, many studies have aimed to improve the energy density of LIBs [74–77]. Along with the introduction of structurally and thermally instable nickel-rich cathodes, attempts have been made to make polyolefin microporous separators thinner. This route toward the development of next-generation LIBs will potentially lead to more serious safety concerns. Thus, it is essential to understand the manufacturing processes and resulting properties of commercial separators. These separators should be carefully designed and finely controlled to guarantee safe functioning in cells and battery performance.

In this review, we first introduced the manufacturing processes of microporous polyolefin separators and presented a brief review of the pore formation mechanism. Although the industrial market is dominated by uniaxially stretched dry-processed PP and biaxially stretched wet-processed PE separators, there may be still room to implement new processes or minor modifications to improve the quality of the separators or raise their productivity. Based on the processing types, the pros and cons of the separators were summarized in Table 1.

Material	PE	РР	PP/PE/PP	PP
Processing Type	Wet, Biaxial	Dry, Uniaxial	Dry, Uniaxial	Dry, Biaxial
Manufacturing cost	Expensive	Cheap	Moderate	Moderate
Simplicity of Manufacturing	Complicated	Simple	Moderate	Complicated
Anistotropy of Micropores	Low	High	High	Low
Shut down function	О	Х	О	Х
Melt down temperature	Low	High	High	High
Tensile Strength (MD)	Strong	Strong	Strong	Moderate
Tensile Strength (TD)	Strong	Weak	Weak	Moderate
Resistance to Puncture	Moderate	Weak	Weak	Weak

Table 1. Properties of microporous polyolefin separators by processing types.

The thermal stability required for safety is highly dependent on the T_m of the constituent substance of the separator, but it can be improved by the use of functional coatings or multilayered structures, which have been widely adopted in industry. Next, we focused on the mechanical and physical properties of separators. The empirical and theoretical backgrounds underlying these properties allowed us to determine several simple correlations, each of which was either universal or type dependent. When comparing microporous separators, the parameters used for characterization need to be chosen with caution. Puncture strength and air permeation (Gurley value) are thickness-dependent parameters, whereas porosity and tensile strength are independent of thickness but still not intrinsic properties of materials. To ensure a fair comparison, thickness-independent values may be useful to judge whether separators satisfy certain requirements regarding the target values for specific applications.

It is hoped that this review can provide insight for the future development of separator membranes and a rough guideline for solid electrolytes, as it is believed these may replace current microporous polyolefin membranes in the future.

Author Contributions: Conceptualization, S.C.M. and J.H.W.; writing—original draft preparation, S.C.M.; writing—review and editing, J.H.W.; funding acquisition, J.H.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2021R1G1A1011510). This work was also supported by Nano-Material Technology Development Program through the NRF funded by the MSIT (2009-0082580).

Conflicts of Interest: The authors declare no conflict of interest.

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