

Deformation and fracture behaviors of microporous polymer separators for lithium ion batteries

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The functionality and reliability of the separator are crucial to the abuse tolerance of a battery since the separator serves as the physical barrier to prevent any contact (short circuit) between the positive and negative electrodes. Therefore, understanding the mechanical behavior, especially the deformation and fracture behaviors of the separator are of great importance for battery design and manufacturing. Here we report the deformation behaviors of five commercially available microporous polymer separators investigated by conventional tensile testing coupled with *in situ* tensile testing under an atomic force microscope. Morphological models were developed to elucidate the tensile deformation mechanisms. For anisotropic separators (Celgard 2325 and 2400) made by the dry process, material direction dictates the significant diversity in overall mechanical integrity of the separator: they have limited mechanical properties when stretched in the transverse direction (TD), whereas they are rather robust when pulled in the machine direction (MD). The anisotropy of these separators is a result of the distinct deformation mechanism of the stacked lamellae in the separator. Separators manufactured by the wet technique (Toray V20CFD and V20EHD, Teijin Lielsort) behaved more biaxially – all mechanical properties were nearly identical in both MD and TD. Moreover, in order to evaluate the fracture properties of these separators, the essential work of fracture (EWF) approach was adopted. The EWF results show that the fracture properties for the dry processed separators also present orientation dependence. When stretching in the MD, the MD-oriented slit-like pores serve as crack tip blunters to inhibit the propagation of cracks whereas the TD-oriented pores exactly facilitate the crack propagation by linking up the pores with the crack tip when stretching in the TD. The same toughening mechanism (tip blunting) was also found in the case of wet processed separators.

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1. Introduction

Because of their superior gravimetric and volumetric capacities, lithium-ion secondary batteries (Li-ion batteries) are increasingly employed in systems such as mobile electronics, space and aircraft power systems, plug-in hybrid electric vehicles (PHEV)/all-electric vehicles (EV), and smart grids.¹ Especially for large format Li-ion batteries, tremendous research efforts have been devoted to improve the energy/power density, high-charge-discharge rates performance, and shelf/cycle life.

However, any reported accidents on Li-ion batteries fires and explosions raise safety concerns and slow down the widespread usage of Li-ion battery technology.² The researches aiming at improving the battery safety can be divided into these categories: (1) developing thermally stable electrodes;^{3–7} (2) developing new all-solid-state electrolyte^{7–9} or lowering the flammability of traditional volatile electrolyte by adding fire-retarded additives into the electrolyte,^{7,10–12} or by replacing/mixing the volatile electrolyte solvent with non-flammable and high chemically stable ionic liquids;^{13–16} and (3) designing safety strategies and devices such as positive temperature coefficient elements, safety vents, and thermal fuses for cells to prevent thermal runaway.^{17–20} In contrast, less attention has been paid to separators, the electrochemically inactive components in liquid electrolyte Li-ion batteries, which prevent any physical contact (internal short circuiting) between the anode and cathode electrodes while permitting the free shuttling of lithium ions in the liquid electrolyte between the electrodes throughout the separator's interconnected porous structure.²¹ The mechanical failure of polymer separators in Li-ion battery cells can result in internal shorting and initiate thermal

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runaway. It has been demonstrated that the tensile stress applied on the separator can be added up to 100 MPa.^{22,23} There is an pressing need to analyze the mechanical behavior of polymer separators (tensile and fracture) and to reveal the structure–property relationship.

According to the material composition, commercial separators can be broadly classified into three types: porous polymer membranes, nonwoven mats, and inorganic composite membranes.²² Owing to their significant advantages such as small thickness, good mechanical strength, excellent electrochemical resistance, and shutdown capability (when overheating occurs the pores are closed *via* melting to shut the battery down), the porous polymer separator membranes are dominating the Li-ion battery separator market.²¹ They are made of polyolefin materials such as polyethylene (PE) and polypropylene (PP) through either a dry process or wet process.

In order to understand the processing, structural and property relationship of membranes, these two processes are briefly overviewed here. In the dry process, the semi-crystalline polyolefin material is first melt-extruded to form films with stacked well-aligned crystallite lamellae arranged in rows with their long axis parallel to the transverse direction (TD). Uniaxial stretching is then applied on the films in the machine direction (MD) to tear apart the lamellae for forming distinct MD-oriented slit-like pores. In the wet process, raw gel-like separator film is first made by extruding a heated homogenous mixture of polymer resins and plasticizers (*e.g.*, paraffin oil, antioxidant, and other additives) into a thin film that is orientated in the MD, which is then followed by extracting the plasticizers from the film with a volatile solvent to leave the polymer pore skeleton in the film which forms the microporous structure. Generally, a biaxial stretching is also employed on the wet processed membrane in both MD and TD after the extraction to enlarge its pore size and increase the porosity. A complete and comprehensive review of battery separators and manufacturing processes can be found in ref. 21 and 22.

In most existing tensile deformation studies on polymer separators, only tensile test approach was used to measure the tensile behavior of the separator by analyzing the stress–strain curves and most their finding about tensile behavior are just the description of the curves.^{24,25} It is our goal to reveal the

underlying structural change in membranes during mechanical deformation. Therefore, to achieve this goal, we have conducted conventional tensile test and *in situ* tensile testing/atomic force microscope (AFM) imaging on five micro-porous polymer separators obtained from three industry leading manufacturers (Table 1 provides the manufacturer specifications for the separators studied.). *In situ* mechanical testing under an AFM is a unique complementary tool to the tensile test that can directly visualize the deformation processes taking place at micrometer scale.^{26,27} The AFM imaging results can thus be directly related to mechanical properties with knowing the precise amount of strain. To the best of authors' knowledge, this is the first time that *in situ* mechanical testing technique has been employed to reveal the tensile behavior of the polymer separator.

By analyzing the stress–strain curves and *in situ* testing results, we found that for the dry processed separators, stretching parallel to the machine direction (MD) leads to lamellae separation coupled with a fibrillation of the amorphous interlamellae phase and is followed by break-up of the crystallite lamellae *via* chain slip mechanism. Stretching parallel to the transverse direction (TD) results in the crystallite lamellae to break up by chain pull-out. However, the wet processed separators show a similar tensile behavior in both MD and TD because of the isotropic surface texture.

The essential work of fracture method has been used in this work to study the fracture behavior of separators and the effect of pores on the toughness of separators. The EWF results show that the dry processed separators have distinctively different fracture mechanical properties in different material orientations (MD and TD). When stretching in the MD, the MD-oriented slit-like pores serve as crack tip blunters to inhibit the propagation of crack whereas the TD-oriented pores exactly expedite the crack propagation by linking up the pores with the crack tip when stretching in the TD. The same toughening mechanism (tip blunting) was also found in the case of wet processed separators.

2. The essential work of fracture

Broberg²⁸ originally proposed the principle behind the essential work of fracture (EWF) approach in 1968, which was then

Table 1 Technical data for commercial Li-ion battery polymer separators used in this study^a

Manufacturer	Celgard	Celgard	Toray	Toray	Teijin
Product name	2325	2400	V20EHD	V20CFD	Lielsort
Material	PP–PE–PP	PP	Unknown polyolefin	Unknown polyolefin	PE substrate coated with fluorine-based compound
Process ^b	Dry	Dry	Wet	Wet	Wet (substrate) and proprietary coating technique
Thickness (μm)	25	25	20	20	15 ^c
Porosity (%)	39	41	42	43	
Puncture strength (g)	380	450	470	310	

^a Data taken from the manufacturers' product brochures except for the thickness of Lielsort. ^b The process type was certified by the AFM surface imaging and tensile test conducted in our study. ^c The thickness was measured by a stylus profiler (Form Talysurf PGI 1240, Taylor Hobson, Ametek Inc.).

extended and applied for fracture characterization of highly ductile polymers in their sheet and film forms by Mai and Cotterell.²⁹ According to the EWF method, the non-elastic region at the crack tip should be partitioned into two regions that is schematically shown in case of a double-edge-notched-tension (DENT) specimen in Fig. 1b: a region named as the process zone where the fracture process takes place, and a neighboring region called plastic zone where further plastic deformation occurs. Therefore, the total work of fracture (W_f) includes both the essential work of fracture (W_e) – the work required to fracture the polymer in its process zone and the non-essential plastic work (W_p) – the dissipative work consumed by multiple deformation mechanisms in the plastic zone. W_f can be then mathematically expressed by equation:

$$W_f = W_e + W_p \quad (1)$$

where W_e is a geometry-independent crack resistance parameter and is proportional to the fracture surface. It thus can be used to describe the fracture property of a material. In contrast, W_p is a geometry-dependent parameter and is proportional to the volume of the plastic zone.^{30,31} Hence, when the specimen's thickness (t) is constant, W_e is proportional to the specimen's ligament length (L) and W_p is proportional to L^2 . In this way, W_f can be given by the following expression:

$$W_f = w_e L t + \beta w_p L^2 t \quad (2)$$

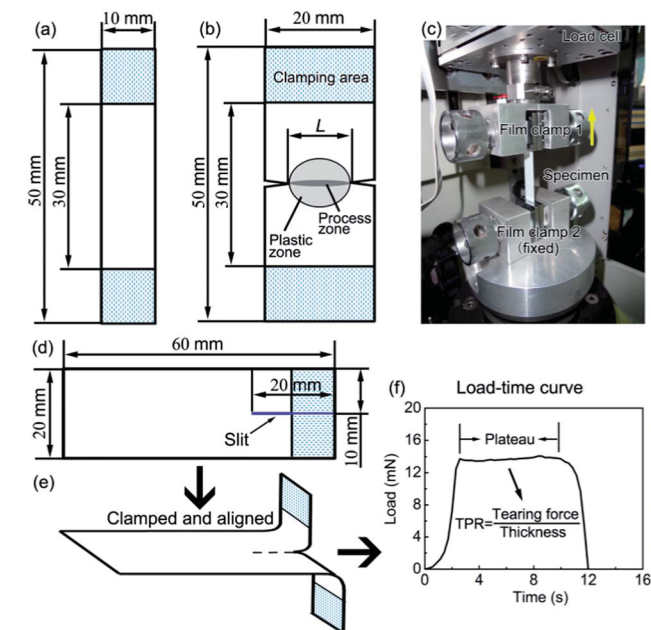


Fig. 1 (a) Tensile test specimen dimension. (b) Schematic diagram showing the process and plastic zones in a DENT specimen for EWF test: L denotes the ligament length. (c) Digital image of the tensile tester. The yellow arrow in (c) indicates the movement orientation of the film clamp 1 during test. (d) Tearing propagation resistance (TPR) test specimen dimension. (e) Schematic diagram of the TPR specimen under testing. (f) Representative load–time curve obtain in TPR test. The tearing force was calculated by averaging the load data displayed as a plateau in the curve.

where w_e and w_p are the specific essential work of fracture and specific non-essential work of fracture, respectively. β is the shape factor depending on the form of the plastic zone. Furthermore, W_f can be rewritten in specific terms when dividing eqn (2) by the fracture surface (ligament section):

$$w_f = W_f / L t = w_e + \beta w_p L \quad (3)$$

in which w_f is the total specific work of fracture. eqn (3) suggests that w_f is a linear function of the ligament length L since w_e , w_p , and β are independent of L . Therefore, w_e and βw_p can be readily determined from the intercept and the slope of the regression line between the data of w_f and L , respectively.³² Note that the W_f can be calculated from the area of the load–displacement curves which can be obtained by the tensile test on DENT specimens (EWF test).

3. Experimental

3.1. Test specimens

Fig. 1a shows the tensile test (TT) specimen geometry: width and length are 10 and 50 mm, respectively. The original gauge length for each specimen was recorded as the distance between the top and the bottom clamps (30 mm). To identify isotropic conditions of each separator, the tensile tests were carried out in both machine direction (MD) and transverse direction (TD). The TT specimens used for the tensile tests in the MD (MD-TT) were cut with the gauge length direction (the stretch direction) parallel to the MD whereas the ones tested in the TD (TD-TT) were prepared with the gauge length direction perpendicular to the MD (parallel to the TD). The double-edge-notched-tension (DENT) specimen dimension (20 mm in width and 30 mm in gauge length) shown in Fig. 1b was selected for the quasi-static fracture toughness measurements. The ligament lengths L used were: 3, 5, 8, 12, 16, 18 mm. Because of the tremendous mechanical difference between the MD and TD of both Celgard 2325 and Celgard 2400, the fracture toughness characterization was performed in both MD and TD for these two separators, while other separators were only tested in the MD. Specimen preparation is very critical to achieve accurate and reproducible measurements. A sharp razor blade was used to cut specimens to different dimensions and open notches for DENT specimens. For Celgard 2325 and Celgard 2400 DENT specimens, the notches in DENT specimens in the TD (TD-DENT) were introduced parallel to the MD whereas the ones in DENT specimens in the MD (MD-DENT) was cut perpendicular to the MD.

3.2. Tensile and EWF testing

Tensile tests and EWF tests were performed with a CETR Tribometer (Bruker Corp.) equipped with 50 N and 100 N load cells under ambient conditions (temperature in the range of 22–26 °C.). The crosshead speed was set at 6 mm min^{−1} for all samples in both tensile and EWF tests, whereas the loads (F) on the MD-TT and MD-DENT specimens for Celgard 2325 and Celgard 2400 were recorded by the 100 N load cell; the loads on all the other test specimens were recorded using the 50 N load cell to achieve a higher precision when measuring small loads.

For the measurement of the tensile properties, five TT specimens were tested for each separator in both MD and TD. To obtain the linear regression of the EWF data, a minimum of six DENT specimens were tested at each ligament. Both TT and DENT specimens were tested up to complete failure. As denoted by the yellow arrow in Fig. 1c, the upward displacement of the moving film clamp 1 was recorded by the Tribometer during test.

3.3. Morphology imaging

A Dimension Icon atomic force microscope (AFM, Bruker Corp.) was employed to image the separators' surfaces. A silicon tip (BudgetSensors TAP300-G, Innovative Solutions Bulgaria Ltd.) with a nominal radius less than 20 nm was used. The AFM was operated under tapping mode at a constant scan rate of 0.5 Hz. The separator samples for the AFM imaging, in the form of 10 mm × 10 mm, were cut using a razor blade. Each sample was glued to a steel sample puck (12 mm in diameter) with superglue at the sample's four corners to prevent vibration-caused image distortions.

3.4. *In situ* tensile testing and AFM imaging

A custom built computer-controlled micro-tensile stage was used to perform *in situ* tensile tests on V20EHD (in the MD) and 2400 (in both TD and MD) TT specimens under an AFM (Dimension 3100; Digital Instruments). The stage has a load resolution of 0.1 N and a displacement resolution of 0.2 μm. Once the TT specimen was set and gripped in the tester, the tensile test was carried out by incremental displacement steps. The minimum strain step was $1.2\% \times 10^{-2}$. The AFM tapping mode with a silicon tip (BudgetSensors TAP300-G, Innovative Solutions Bulgaria Ltd.) was used to *in situ* image surface topography of the specimen during tensile loading at a constant scan rate of 0.6 Hz. Images of the same control area (only for the 2400 MD-TT specimen), which was chosen at the center of the specimen, were taken before and after stretching the specimen with the help of the attached optical microscope. Because the other specimens (V20EHD MD-TT and 2400 TD-TT) involved large deformations, which made it very difficult to perform *in situ* imaging, we only scanned the areas of interest on these specimens rather than the same control areas during tensile loading.

3.5. Tear propagation resistance testing

Tear propagation resistance (TPR) for separators listed in Table 1 were measured by the Tribometer equipped with 500 mN and 5 N load cells at a crosshead speed of 200 mm min⁻¹ using the trouser tear method.³³ The specimen shape and dimension as well as the length of the slit located in the center of the specimen are shown in Fig. 1d. Two groups of specimens for each separator with their long axis parallel (MD TPR specimen) and perpendicular (TD TPR specimen) to the MD were prepared. After the two legs of the test specimen were carefully clamped and aligned (Fig. 1e), the TPR test was then started and the load was recorded real time until the entire unslit part was torn. Tear force was determined by averaging the load data

shown as a plateau in load–time curve, as representatively illustrated in Fig. 1f. The TPR was then calculated by dividing the tear force by specimen thickness. Five specimens were tested for each separator in both MD and TD. The TPR in the MD was measured by testing the MD TPR specimens while TD TPR was tested on the TD TRP specimens.

4. Results and discussion

4.1. Morphological properties

Fig. 2 shows the 5 μm × 5 μm AFM height images of the separators. It can be observed that the Celgard products—both 2325 and 2400 have a similar anisotropic topography with slit-like pore structures, as shown in the insets of Fig. 2a and b, which was induced by the dry process. The slit-like pores are uniformly machine direction (MD)-oriented and each pore is entrapped by two nanofibrils as indicated by the arrow in white color in the inset of Fig. 2a. The Toray products manufactured by the wet process—the V20CFD and V20EHD also show little discrepancy in their morphologies. However, unlike the Celgard products, they have rather isotropic textures and remarkably larger interconnected spherical or elliptical shaped pores as illustrated in Fig. 2c and d. Fig. 2e shows the surface topography of Teijin's Lielsort separator. As introduced in the manufacturer's brochure, this separator uses a conventional porous PE separator, manufactured by the wet process (later confirmed by the tensile test), as substrate, onto which fluorine-based compound is coated using a proprietary coating technique.

However, it can be seen that, in Fig. 2e, no large spherical shaped porous features were found for the PE substrate. Instead, smaller and uniform chestnut-like porous structures were observed. Therefore, it can be inferred that these porous structures belong to the coating, which is thick enough to completely cover the PE separator substrate.

4.2. Tensile properties

Separators should be mechanically strong enough, especially in the MD, to withstand the tension stress induced by the MD winding operation during cell assembly. The tensile test is a practically viable method to evaluate the robustness of a separator. In this study, we have carried out tensile tests on all commercial separators listed in Table 1 in both MD and TD to obtain engineering stress–strain curves. The engineering stress, σ , is defined as

$$\sigma = F/A \quad (4)$$

in which F is the load on the separator TT specimen and A is the original TT specimen cross section area. The percentage engineering strain, ϵ , is defined as

$$\epsilon = (\Delta/l_0) \times 100\% \quad (5)$$

where l_0 is the original gauge length (30 mm in our study), Δl is the elongation of the specimen, which is approximately equal to the upward displacement of the moving film clamp 1 (Fig. 1c).

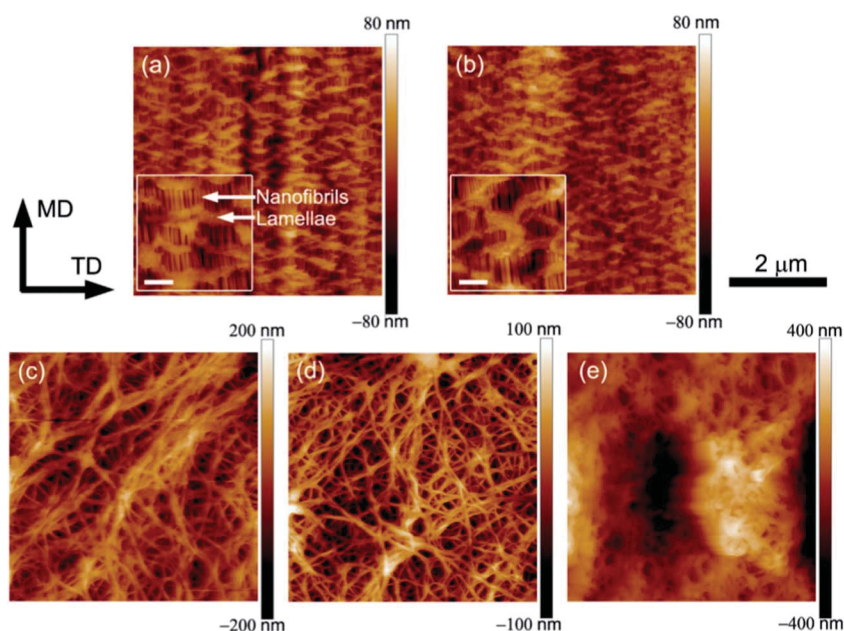


Fig. 2 AFM height images for separators (a) Celgard 2325, (b) Celgard 2400, (c) Toray V20CFD, (d) Toray V20EHD, and (e) Teijin Lielsort fluorine-based resin coated separator. The insets with a scale bar of 250 nm in the (a) and (b) are their corresponding high magnification height images. The nano-sized fibrils and lamellae are pointed out by white arrows in the (a) inset. The arrows denoted by MD and TD indicate the two distinct material directions: the machine direction (MD) and transverse direction (TD), respectively.

Here it should be noted that the displacement of the moving film clamp actually consists of the elongation of the specimen (Δl) and the elongation due to the system compliance which is the elongation of a load weighing system, clamps, and clamp penetration per unit force. However, in our study the system compliance induced displacement is negligible comparing to the large deformation of the soft separators. Therefore we use the clamp displacement as the elongation of the specimen. Consequently, this approximation of the Δl may result in a slightly larger deformation strain and accordingly lower Young's modulus.³⁴

A group of representative engineering stress-strain curves for the separators in both MD and TD were plotted in Fig. 3. The MD and TD tensile deformations for the Celgard products (2325 and 2400) made by the dry process are shown in Fig. 3a and b, respectively. The same forms of data for the Toray products (V20CFD and V20EHD) manufactured by the wet process and for the Teijin Lielsort sample are shown in Fig. 3c and d. These data clearly show the remarkable differences in the tensile mechanical properties of these separators, particularly those made by the dry process and by the wet process and those fabricated by the dry process in the MD and TD. The mechanical properties of Young's modulus, tensile strength, strain that non-linearity occurred, and break strain determined from stress-strain curves are listed in Table 2.

4.2.1. MD and TD tensile deformation of the separators made in the dry process. The MD stress-strain curves of both dry processed Celgard 2325 and 2400 separators in Fig. 3a are similar to the typical hard elastic polymers showing the six regimes of behavior as elasticity (linear, non-linear), yielding, strain softening, cold drawing, strain hardening, and failure.³⁵

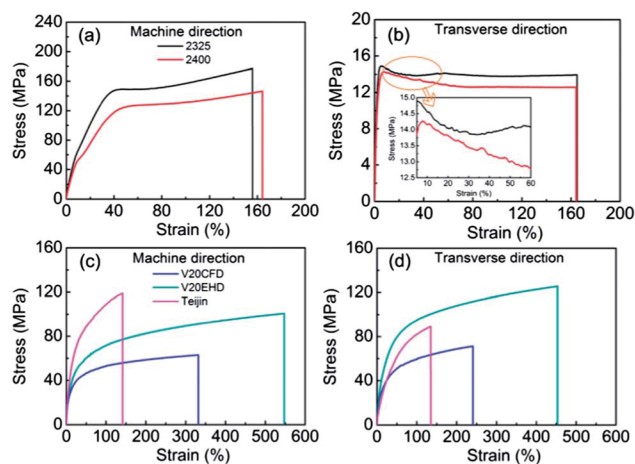


Fig. 3 Engineering stress-strain curves of separators. (a) and (b) show curves for Celgard 2325 and 2400 in the machine direction and transverse direction, respectively. The inset in (b) is the enlarged view of the region indicated by the orange colored ellipse. (c) and (d) give curves for Toray V20CFD, V20EHD, and Teijin in the machine and transverse direction, respectively.

However, the strain softening did not occur in the third regime of 2325 and 2400 MD curves. Instead, the cold-drawing behavior, appearing as a short horizontal plateau (elongation at constant stress) in each MD stress-strain curve, took place immediately after yielding. For the TD deformations in Fig. 3b, all Celgard products displayed a very different yielding style, a sharp yield peak, compared with the case of the MD deformation, and necked at very early stages of the deformation ($< \sim 8\%$).

Table 2 Mechanical properties of the separators

Separator	Direction	Measured modulus ^a (MPa)	Tensile strength (MPa)	Strain that non-linearity occurred (%)	Strain at break (%)
2325	MD	935 ± 43	175.2 ± 9.1	0.79	155.9
	TD	510 ± 24	14.7 ± 1.9	0.61	164.9
2400	MD	873 ± 37	146.5 ± 7.4	0.85	164.3
	TD	502 ± 28	13.4 ± 2.2	0.76	164.2
V20CFD	MD	675 ± 25	65.3 ± 5.3	0.68	333.2
	TD	781 ± 39	72.6 ± 6.7	0.72	241.5
V20EHD	MD	696 ± 48	102.7 ± 7.8	0.65	547.7
	TD	823 ± 52	127.8 ± 9.1	0.87	453.2
Teijin	MD	733 ± 41	120.6 ± 9.6	0.63	142.2
	TD	622 ± 36	90.1 ± 8.5	0.54	134.9

^a The Young's modulus was calculated from the slope of the linear stress-strain curve in the strain range of 0–0.5%.

They then underwent strain softening to different amount of strains: 90% for 2325 and 65% for 2400. Particularly, for 2325 TD, deformation strain softening was interrupted by the strain hardening in the strain range from 30% to 55%. Subsequently, they showed a large amount of cold drawing. At the last stage of deformation, the two TD samples broke in a “brittle” fashion without strain hardening. Also, it should be noticed that the uneven feature of the TD curves at the region of the strain softening, which is magnified in the inset of Fig. 3b, shows a stick-slip phenomenon.

The pronounced variations in the mechanical properties for the dry processed separators in the MD and TD can be explained by their morphology evolutions during the deformation process. We thus carried out *in situ* tensile and AFM imaging tests (*in situ* tensile/AFM testing) on a dry processed separator—the Celgard 2400 in both MD and TD, of which the results are shown in Fig. 4b–g and 5d–g, respectively. Deriving from these *in situ* tensile/AFM testing results, we established a morphological model to schematically illustrate the deformation process, as sketched in Fig. 4a (stretched in the MD) and Fig. 5c (stretched in

the TD). The proposed model (unit model) actually mimics the basic surface texture unit formed by two adjacent stacked crystallite lamellae rows and a bundle of nano-sized fibrils between them. And here it should be noted that the internal structure of the dry-processed separator can also be viewed as a multilayered structure, into which basic surface texture units (unit model) are stacked layer by layer in the thickness direction, basing on the cross section scanning electron microscopy observation in ref. 36. Furthermore, based on Love's X-ray diffraction observation²⁵ that separators made by the dry process have a high degree of crystallinity the fibril was presumably considered as an crystalline phase, and a very small amount of the amorphous phase was only present in the interlamellar spacing (not shown in the unit model).³⁵ In the following paragraphs, the deformation process and mechanisms in the MD and TD will be discussed separately by means of combining the unit model with the *in situ* tensile/AFM testing results.

When the separator was extended along the MD, the fibrils effectively “shared” and “carried” the load. They consistently elongated themselves to accommodate the deformation. This is

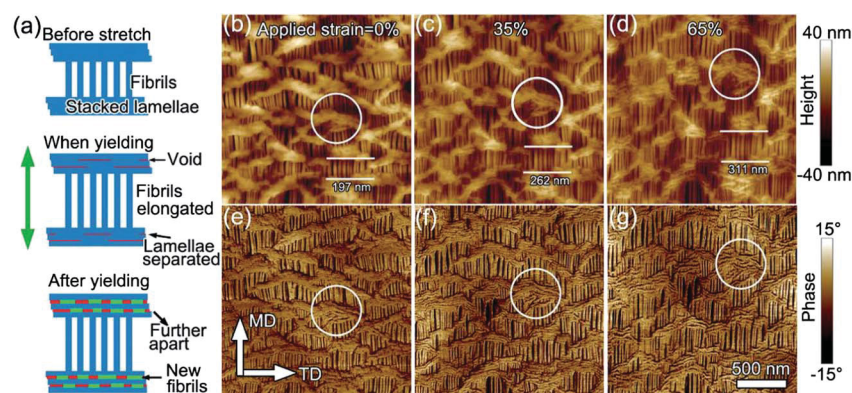


Fig. 4 Deformation of the lamellae and nano-sized fibrils of the 2400 separator in the MD during tensile test. (a) Schematic illustration of the MD tensile deformation process: fibrils were elongated at the early stages of deformation; lamellae began to separate when yielding; once the yield point was passed, a fibrillation of the amorphous interlamellar material took place and new fibrils bridged the voids generated by the lamellae separation and rotation. (b)–(d) AFM height images of the same scanning area in the specimen (b) under 0% (un-stretched), (c) 35%, (d) 65% engineering strain, respectively. (e) and (f) Phase images corresponding to (b)–(d). Green arrows on the left indicate the orientation of applied tensile strain.

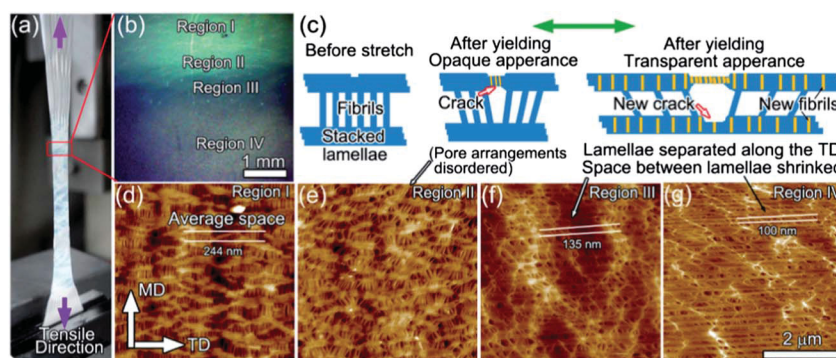


Fig. 5 TD tensile deformation of the lamellae and nano-sized fibrils of the 2400 separator. (a) Digital image of the TD-TT specimen during testing. Plastic deformation occurs faster in localized regions, forming the crazes. (b) Optical image of a craze, which is artificially divided into four regions: Region I–IV. Region I shows a conventional “un-stretched”-like surface; Region III shows a “whitening” opaque appearance; Region II is the transition region between the Region I and III; Region IV has a transparency appearance. (c) Schematic illustration of the TD tensile deformation process: the crystalline lamellae rows break-up easily due to the small overall effective area of surface under tension as well as the cracks induced by the slit-like pores; crystalline lamellae break up or rupture *via* chain pull-out and the pulled out polymer chain forms the new fibril (denoted by the line in yellow color). (d)–(g) AFM height images of Region I–IV, respectively. Green arrows above (c) point out the orientation of applied tensile strain.

evident from the results of the *in situ* tensile and AFM imaging test on the 2400 separator shown in Fig. 4b–g. As point out by the white line in Fig. 4b–d, the average length of the bundle of fibrils steadily increased from 197 nm to 311 nm when the separator was strained to 65%. On the other hand, when stretched upon the yield point (~35% strain), the lamellae rows began to separate, inducing the separation of the stacked lamellae, as denoted by white circles in the AFM image of MD deformed 2400 separator in Fig. 4c (height image) and 4f (phase image). Fig. 4a schematically shows this process by highlighting the voids generated by stacked lamellae separation in red color. As the deformation further proceeded, a fibrillation of the amorphous interlamellar material took place, denoted by the green lines in the model (Fig. 4a), bridging the voids generated by the lamellae separation and rotation (Fig. 4d and g). At this stage, these fibrillation behaviors showed a large strain under a constant stress in the MD stress–strain curves. Again, owing to the paucity of amorphous phase, the fibrillation process did not sustain for a wider strain range—process just stopped until the amorphous phase was depleted, resulting in a short plateau in the MD stress–strain curves in Fig. 3a. To accommodate the further stretching strains, the crystalline lamellae were then deformed through a chain slip mechanism, which caused the large degree of strain hardening as shown in the MD stress–strain curves.^{37,38}

Fig. 5c schematically demonstrates the TD deformation process of the unit model. When the TD stretching started, the lamellae rows mainly carried the load and were elongated accordingly. As for the fibrils, since they were more or less perpendicular to the direction of the applied strain (TD), they carried the least load. Thereby the overall effective area of surface under tension is significantly small. Moreover, the slit-like pores between fibrils practically served as notches in this case, which can readily initiate cracks in the lamellae rows, especially into the thinner ones, causing the quick localized break-up of the lamellae rows. This crack-induced break-up (stretching) is

schematically illustrated in Fig. 5c, and the distorted fragments of lamellae rows in the AFM height (Fig. 5e) image also provided a very convincing evidence. The distorted lamellae row pattern also suggests another deformation mechanism—the fragment rotation, which, along with the localized lamellae row break-up, can effectively dissipate the tension energy and expel the strain concentration. This can be treated as a strain-softening event in the TD stress–strain curves (Fig. 3b). Furthermore, each lamellae row fragment still connected to each other by the new fibrils generated during breakup, which can be clearly observed in Fig. 5f when sample was further strained. Here it should be noted that although each AFM image was denoted with a region number like, Region I–IV, to correspond to the position where AFM imaging was performed in the optical image (Fig. 5b), all the AFM images together exactly depict the morphology evolution of an localized area, at least for the “transparent” area (Fig. 5a), in the sample during the TD plastic deformation process. Therefore, the separator sample yielded sharply after a very limited amount of elastic deformation of the crystallite lamellae, followed by the crystalline lamellae break-up or rupture *via* chain pull-out.³⁸ These pulled out polymer chains recrystallized and realigned parallel to the TD and were finally assembled into new fibrils as denoted in yellow color in the unit model (Fig. 5c), which gave rise to a long horizontal plateau in the TD stress–strain curve in Fig. 3b. Moreover, as pointed out previously, the stick-slip phenomenon occurs immediately after yielding. We speculate that this stick-slip behavior is the reflection of the initial expansion of the neck along the entire length direction of the sample on the curves. That is, in the early stages of deformation after yielding, the inner stress underwent accumulation (concentration) in the necked region and relaxation *via* triggering the plastic deformation to form a few localized deformed regions as shown in the optical image of Fig. 5b, which resulted in a dramatic stress fluctuation. As the number of localized deformed region increases (Fig. 5a), the fluctuation was suppressed and showed a stable horizontal plateau in the curves.

4.2.2. Tensile deformation of the separators made in the wet process. Since the tensile properties depends on the morphology of the membranes, which are determined by manufacturing process, we see different mechanical behavior in separators made in the wet process, as presented in Fig. 3c and d. First of all, unlike those of the dry processed films, the MD and TD stress-strain curves of each wet processed separator are quite similar, exhibiting a nearly isotropic mechanical property. Therefore, when related to the separators' isotropic morphologies discussed in Section 4.1, it is not hard to draw a conclusion that the texture of a film largely governs its mechanical properties. Another difference from those “hard elastic” dry processed separators, the wet processed separators showed a behavior similar to the tensile deformation for a ductile material. For small strains (*e.g.* less than 0.68% for V20CFD), the deformation was elastic and can be reversed if the load was removed. At higher strains, nearly perfect plastic flow behavior occurred. Moreover, at the last stage of deformation, the tensile stress in each wet processed sample reached a maximum at fracture and the samples failed in a “brittle” fashion. This is quite different from the behavior of a typical ductile material, which generally undergoes strain softening before rupture due to the initiation of the necking.

The wet processed separators actually also behaved distinctly in the macroscopic scale. They necked at very early stages of the deformation (may be at the strains where non-linearity started); and the necking took place uniformly along the gauge length unlike other materials which prefer to initiate a localized necking and then expand it along the entire length. To elucidate the deformation process and the distinct mechanical behaviors, we performed *in situ* tensile/AFM test on a representative wet processed separator—the V20CFD. The AFM height image of un-stretched and stretched (200% engineering strain) sample surface are presented in Fig. 6a and c, respectively. It can be seen from the figures, the pore structures in the separator are hardly found after stretching, leaving a condensed/stacked “lamellae”-like structures that are well oriented along the direction of applied strain (SD). We then developed a model, schematically drawn in Fig. 6b, based on these testing results. During elongation, the fibers surrounding large spherical shaped pores were stretched and re-oriented with their length directions along the SD. Accordingly, the shape of pores changed from the spherical to the elliptical whose major axis

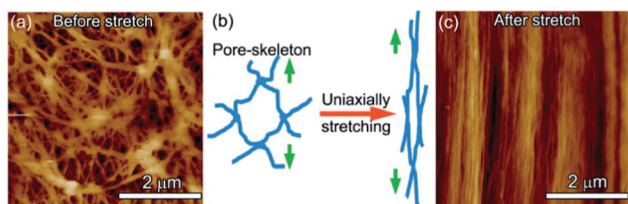


Fig. 6 Deformation of the micropores of the separator V20CFD in the MD during tensile test. AFM height image of the (a) un-stretched and (c) stretched (200% engineering strain) separator, respectively. (b) Schematic illustration of the micropores deformation process. Green arrows in (c) denote the orientation of applied tensile strain.

was parallel to the SD. As a consequence, the dimension in the direction perpendicular to SD for most of the pores decreased, leading to the uniform necking over the entire gauge length of the sample. As the tensile deformation continued, the pores were almost compressed to disappear. Thus, highly oriented fibers were stacked together to show a condensed “lamellae”-like morphology as shown in Fig. 6c. These observations attest to the ductility of the structure as a whole during deformation: at the initial stage of deformation, the structure was mechanically robust and behaved elastically; as more strain was applied, it exhibited perfect plastic deformation flow *via* pore collapsing. Finally, this condensed sample was deformed further to fracture.

4.3. EWF and tear propagation resistance test results

To characterize the fracture toughness of the separators, we carried out EWF tests on both dry processed and wet processed separators. The load-displacement curves for the DENT specimens with a range of ligaments (*L*: 3–18 mm) are demonstrated in Fig. 7. Because of their orientation dependence of the

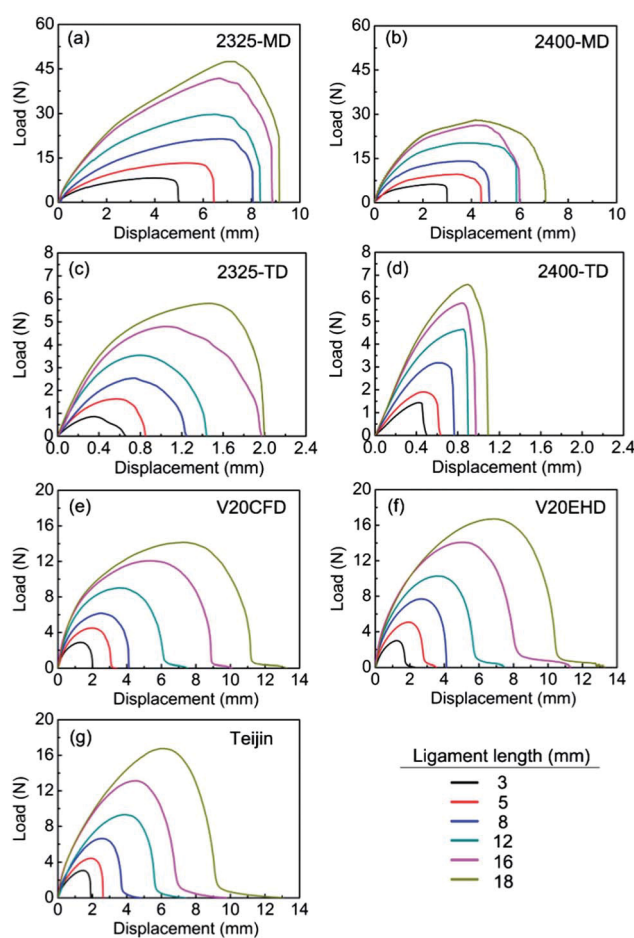


Fig. 7 Load-displacement curves for the DENT specimens of (a) Celgard 2325 and (b) Celgard 2400 in the machine direction (MD); (c) Celgard 2325 and (d) Celgard 2400 in the transverse direction (TD); (e) Toray V20CFD, (f) Toray V20EHD, and (g) Teijin in the MD. With increasing ligament length, both the related load and displacement increased.

mechanical properties, separators made by the dry process were tested in both MD and TD. Shown in Fig. 7a and c are the curves for Celgard 2325 in the MD (2325-MD) and TD (2325-TD), respectively. The same forms of data for Celgard 2400 in the MD (2400-MD) and TD (2400-TD) are presented in Fig. 7b and d. All other separators listed in Table 1 (V20CFD, V20EHD, and Teijin) were tested only in the MD due to their nearly isotropic mechanical properties. The curves for these wet processed films are shown in Fig. 7e, f, and g, respectively. As can be observed from Fig. 7, all the sets of load-displacement curves were geometrically self-similar with each other, indicating that the fracture mechanism was independent of the ligament length. Moreover, the ligaments were fully yield before the propagation of the cracks at the maximum stretching load, which exactly met the EWF prerequisite.²⁹

The area under each of the load-displacement curves of Fig. 7 is equal to the total work of fracture (W_f) for each of the DENT specimens, which was divided by the cross-section area of the ligament to obtain the total specific work of fracture (w_f). The values of w_f were plotted against those of ligament length (L) in Fig. 8, and what followed was the linear fitting the data of w_f and L for each DENT specimen. As shown in Fig. 8, a good linear regression of the w_f versus L is achieved. The specific essential work of fracture (w_e) and the specific non-essential term (βw_p) were thus determined as the intercept at zero ligament length and the slope of the regression line, respectively, according to eqn (3). Table 3 summarizes the parameters w_e and βw_p for each DENT specimen. It is apparent that the fracture

Table 3 Parameters of the specific work of fracture (specific essential w_e and non-essential βw_p) of separators

Separator	Direction	w_e (kJ m ⁻²)	βw_p (kJ m ⁻³)
2325	MD	13.777	441.35
	TD	0.9041	2.5788
2400	MD	11.266	185.18
	TD	0.3772	4.8979
V20CFD	MD	16.265	15.508
V20EHD	MD	17.941	5.951
Teijin	MD	12.163	27.131

mechanical properties for the dry processed separators (Celgard 2325 and 2400) significantly depend on the texture orientation: the essential works of fracture in the MD are an order of magnitude larger than those for these separators in the TD; and the differences in the non-essential terms (βw_p) between the MD and TD are even larger, *e.g.* the βw_p for 2325 is 441.35 kJ m⁻³ in the MD whereas only 2.5788 kJ m⁻³ in the TD. This again is due to the slit-like microporous structure nature of this kind of separator. As pointed out in the unit model proposed in Section 4.2.1, the stress concentrators – the slits (pores) that are parallel to the direction of the ligament length (direction of crack growth) will readily trigger the localized plastic deformation of the stacked lamellae when the TD-DENT specimen is stretched, which thus causes a very small plastic work of fracture. Furthermore, the presence of TD-oriented slit-like pores in the

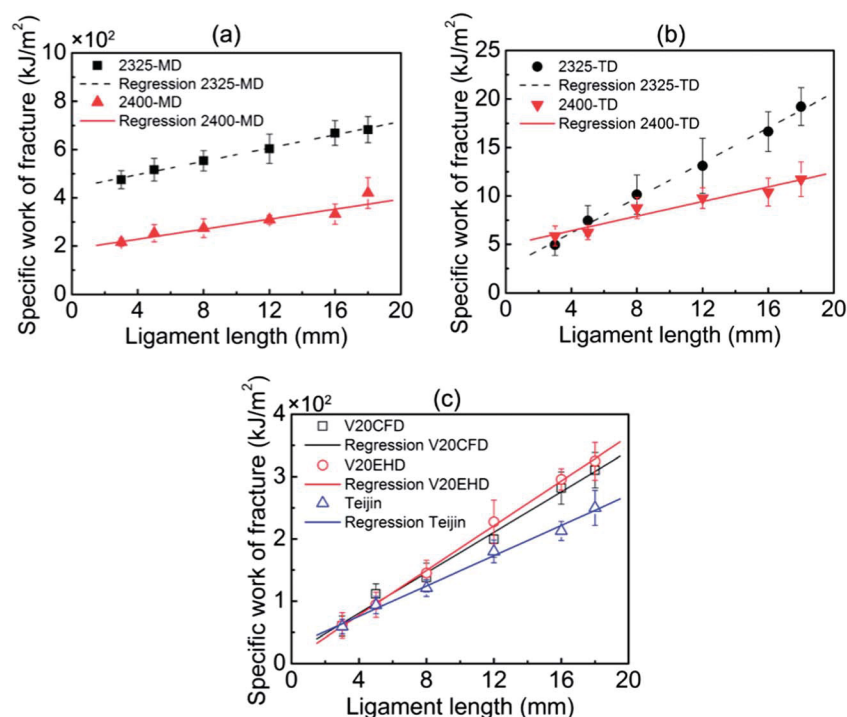


Fig. 8 Specific work of fracture vs. ligament length of (a) Celgard 2325 and 2400 in the machine direction (MD), (b) Celgard 2325 and 2400 in the transverse direction (TD), and (c) Toray V20CFD, V20EHD, and Teijin in the MD. The inset in (a) shows (left) digital image of the fractured 2400-MD DENT specimen with a ligament of 5 mm and (right) schematic sketch of the crack path (dashed line in magenta color) along the direction of applied stress in the specimen.

process zone (Fig. 1b) also greatly expedites the crack propagation by linking up the pores with the tip of the crack. As a consequence, the fracture surface mainly consists of the surfaces of preexisting pores which do not require any fracture energy. Thus the total work of fracture (W_f) of each TD-DENT specimen consumed is very low. In contrast, for the MD-DENT specimen made by the dry process, the MD-oriented slit-like pores have their length directions perpendicular to the direction of crack growth. Therefore, when the MD-DENT specimen is stretched, these slits exactly play a critical role in the inhibiting of crack propagation (crack tip blunting). That is, when a crack meets a slit-like pore in the porous separator, the crack tip becomes blunt, which decreases the stress-concentration at the crack tip and increases the total work of fracture (W_f). As a further proof for the above explanation for the orientation dependence of the fracture mechanical properties, the tear propagation resistances (TPR) in the MD are overwhelmingly larger than those in the TD for all dry processed separators, as shown in Fig. 9.

For the separators manufactured by the wet process (Toray V20CFD, V20EHD, and Teijin Lielsort), the Toray products show a similar specific essential work of fracture (w_e) while the Teijin product has a slightly smaller w_e and a larger specific plastic work of fracture (βw_p) comparing to the Toray counterparts. This variance in fracture mechanical properties can be presumably ascribed to the crack bridging mechanism – the coating that is conformably formed on the Teijin separator surface bridges the crack to slow the crack expansion during EWF test. The slow propagation of crack thus allows more plastic deformation and therefore higher βw_p . The fracture mechanical properties also show a dependence upon manufacturing process. The separators (MD) made by the dry process has a larger βw_p than the wet processed ones even though both dry and wet processed separators possess a similar w_e . The similarity of w_e between the dry and wet processed separators may be due to the same material toughening mechanism (the tip blunting) since the wet processed separators have nondirectional round pores as the crack tip blunters during EWF test. Whereas the difference in the specific plastic work of fracture (βw_p) is possibly attributed to the mechanical property discrepancy of the non-porous phase in separators – the more robust non-porous phase generally undergoes more

plastic deformation at the crack tip and in the plastic zone, inducing a higher value of βw_p . To qualitatively compare the mechanical property difference between the two kind of separators, we can refer to the tensile test results (Fig. 3 and Table 2), which suggest that the tensile strength of fibers surrounding round-like pores in the wet processed separator is weaker than that of the nanosized fibrils and stacked lamellae in the dry processed separator. Moreover, the TPR test results also decisively demonstrated the remarkable differences in the mechanical properties for non-porous phase. As shown in Fig. 9, the TPR for each dry processed separator (MD) is almost two order magnitude larger than that for any wet processed counterpart.

5. Conclusions

Tensile behaviors for separators manufactured by both dry and wet process were analyzed based on the results of tensile tests and *in situ* tensile testing and AFM imaging. Accordingly, morphological models have been developed to elucidate the tensile deformation process. For the dry processed separators, stretching parallel to the machine direction (MD) leads to lamellae separation coupled with a fibrillation of the amorphous interlamellae material and is followed by break-up of the crystallite lamellae *via* chain slip mechanism. Stretching parallel to the transverse direction (TD) results in the crystallite lamellae to break up by chain pull-out. However, the wet processed separators shows a similar tensile behavior in both MD and TD because of the isotropic surface texture: stretching causes the round-like pores to collapse from the initial stage of deformation and is followed by a failure in a “brittle” fashion.

The essential work of fracture (EWF) concept has successfully been applied to the commercial microporous separators. The EWF results show that the dry processed separators have distinctively different fracture mechanical properties in different material orientations (MD and TD). When stretching in the MD, the MD-oriented slit-like pores serve as crack tip blunters to inhibit the propagation of crack whereas the TD-oriented pores exactly facilitate the crack propagation by linking up the pores with the crack tip when stretching in the TD. The same toughening mechanism (tip blunting) was also found in the case of wet processed separators. The findings in this study provide new guidelines for optimizing separator manufacturing process and valuable mechanical data for modeling the reliability of polymer separators in lithium-ion batteries.

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Notes and references

- 1 J. Liu, *Adv. Funct. Mater.*, 2013, **23**, 924–928.

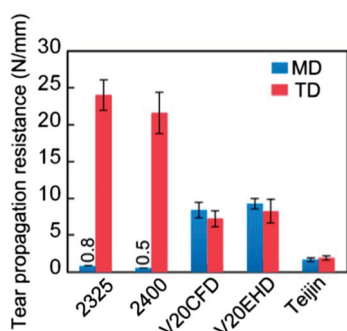


Fig. 9 Tear propagation resistance of separators listed in Table 1 in both MD and TD.

- 2 Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun and C. Chen, *J. Power Sources*, 2012, **208**, 210–224.
- 3 N. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y. K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho and P. G. Bruce, *Angew. Chem., Int. Ed.*, 2012, **51**, 9994–10024.
- 4 O. Park, J. Lee, M. J. Chun, J. T. Yeon, S. Yoo, S. Choi, N. Choi and S. Park, *RSC Adv.*, 2013, **3**, 2538–2542.
- 5 A. Jain, G. Hautier, C. Moore, B. Kang, J. Lee, H. Chen, N. Twu and G. Ceder, *J. Electrochem. Soc.*, 2012, **159**, A622–A633.
- 6 M. Zhou, L. Zhao, T. Doi, S. Okada and J. Yamaki, *J. Power Sources*, 2010, **195**, 4952–4956.
- 7 J. B. Goodenough and Y. Kim, *Chem. Mater.*, 2010, **22**, 587–603.
- 8 S. Ramesh and S. Lu, *J. Mol. Liq.*, 2013, **177**, 73–77.
- 9 X. Zuo, X. M. Liu, F. Cai, H. Yang, X. D. Shen and G. Liu, *J. Mater. Chem.*, 2012, **22**, 22265–22271.
- 10 S. S. Zhang, *J. Power Sources*, 2006, **162**, 1379–1394.
- 11 S. Kaymaksiz, F. Wilhelm, M. Wachtler, M. Wohlfahrt-Mehrens, C. Hartnig, I. Tschernych and U. Wietelmann, *J. Power Sources*, 2013, **239**, 659–669.
- 12 G. Nagasubramanian and K. Fenton, *Electrochim. Acta*, 2012, **101**, 3–10.
- 13 A. Lewandowski and A. Świdorska-Mocek, *J. Power Sources*, 2009, **194**, 601–609.
- 14 K. Zaghib, M. Dontigny, A. Guerfi, J. Trottier, J. Hamel-Paquet, V. Gariépy, K. Galoutov, P. Hovington, A. Mauger, H. Groult and C. M. Julien, *J. Power Sources*, 2012, **216**, 192–200.
- 15 S. Menne, R. S. Kühnel and A. Balducci, *Electrochim. Acta*, 2013, **90**, 641–648.
- 16 J. C. Forgie, S. El Khakani, D. D. MacNeil and D. Rochefort, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7713–7721.
- 17 P. G. Balakrishnan, R. Ramesh and T. Prem Kumar, *J. Power Sources*, 2006, **155**, 401–414.
- 18 G. J. Offer, V. Yufit, D. A. Howey, B. Wu and N. P. Brandon, *J. Power Sources*, 2012, **206**, 383–392.
- 19 X. Jing, H. Banvait, L. Lingxi, C. Yaobin, X. Jian, L. Yadong, W. Meng and C. Jie, *Electric Vehicle Conference (IEVC), 2012 IEEE International*, 2012, 1–5.
- 20 L. Xia, L. Zhu, H. Zhang and X. Ai, *Chin. Sci. Bull.*, 2012, **57**, 4205–4209.
- 21 X. Huang, *J. Solid State Electrochem.*, 2011, **15**, 649–662.
- 22 S. S. Zhang, *J. Power Sources*, 2007, **164**, 351–364.
- 23 D. Ihm, J. Noh and J. Kim, *J. Power Sources*, 2002, **109**, 388–393.
- 24 A. Sheidaei, X. R. Xiao, X. S. Huang and J. Hitt, *J. Power Sources*, 2011, **196**, 8728–8734.
- 25 C. T. Love, *J. Power Sources*, 2011, **196**, 2905–2912.
- 26 X. Li, W. Xu, M. A. Sutton and M. Mello, *Mater. Sci. Technol.*, 2006, **22**, 835–844.
- 27 X. D. Li, W. J. Xu, M. A. Sutton and M. Mello, *IEEE Trans. Nanotechnol.*, 2007, **6**, 4–12.
- 28 K. B. Broberg, *Int. J. Fract. Mech.*, 1968, **4**, 11–19.
- 29 Y. W. Mai and B. Cotterell, *Int. J. Fract.*, 1986, **32**, 105–125.
- 30 F. M. Peres, J. R. Tarpani and C. G. Schönc, *Eng. Fract. Mech.*, 2013, **105**, 136–151.
- 31 A. B. Martinez, J. Gamez-Perez, M. Sanchez-Soto, J. I. Velasco, O. O. Santana and M. Ll MasPOCH, *Eng. Failure Anal.*, 2009, **16**, 2604–2617.
- 32 T. Bárány, T. Czigány and J. Karger-Kocsis, *Prog. Polym. Sci.*, 2010, **35**, 1257–1287.
- 33 ISO standard 6383: Plastics – Film and sheeting – Determination of tear resistance – Part 1: Trouser tear method, 1983.
- 34 A. V. Sergueeva, J. Zhou, B. E. Meacham and D. J. Branagan, *Mater. Sci. Eng., A*, 2009, **526**, 79–83.
- 35 S. Kreitmeier, M. Wittkop, T. Wagner, D. Göritz and R. Zietz, *Colloid Polym. Sci.*, 1995, **273**, 1008–1021.
- 36 P. Arora and Z. Zhang, *Chem. Rev.*, 2004, **104**, 4419–4462.
- 37 P. B. Bowden and R. J. Young, *J. Mater. Sci.*, 1974, **9**, 2034–2051.
- 38 A. Peterlin, *Colloid Polym. Sci.*, 1987, **265**, 357–382.