Strain rate effect and micro-buckling behavior of anisotropic macromolecular separator for lithium-ion battery

W. Q. Hao¹, J. M. Xie¹, X. Zhang², P. Wang^{1,2}, F. H. Wang^{1*}

¹Bi-inspired and Advanced Energy Research Center, Department of Engineering Mechanics, Northwestern Polytechnical University, Xi'an, 710129 Shaanxi, China

²Tubular Goods Research Institute, China National Petroleum Corporation, Xi'an, 710065 Shaanxi, China

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Abstract. High tensile strength and good toughness play an important role in improving the mechanical performance of separator films, such as resistance to external force, service life and so on. In the present research, the strain rate effect and micro-buckling behavior of two types of anisotropic separators for lithium-ion battery (LIB) under different strain rates are investigated. The results conclude that the anisotropy effect and strain rate effect are displayed obviously along the machine direction (MD), diagonal direction (DD) and transverse direction (TD). The constitutive relationship with a strain rate of anisotropic macromolecular separator for LIB is $\ln\{\epsilon/\sigma - 1/(E_0[1 + \lambda_1(\ln \dot{\epsilon} - \ln \dot{\epsilon}_0)])\} = \kappa \ln \epsilon - \ln E_0 - \ln[1 + \lambda_1(\ln \dot{\epsilon} - \ln \dot{\epsilon}_0)]$. The separator has high tensile strength along MD and good toughness along DD and TD. The maximum error of strain rate strengthening coefficient $\lambda_1 = \partial E(\dot{\epsilon})/(E_0 \partial \ln \dot{\epsilon})$ and $\lambda_2 = \partial \sigma_s(\dot{\epsilon})/(\sigma_{s0} \partial \ln \dot{\epsilon})$ about the material parameter is less than 15%. Finally, the critical stress $\sigma_{x,crit} = -Ek\pi^2(t/B)^2/12(1 - \mu^2)$ characterizing the micro-buckling behavior of macromolecular separators are proposed and discussed. The critical stress error rates are approximately $Error = 2\text{--}7\%$ compared with experimental results. This research provides guidance to improve the mechanical property of anisotropic separator and addresses the safety of LIB.

Keywords: polymer membranes, macromolecular separator, lithium-ion battery, micro-buckling, strain rate effect

1. Introduction

Lithium-ion battery (LIB) has received considerable attention as a popular electrochemical energy source for a wide range of applications, including electric vehicles and cell phones, and so on [1, 2]. Many researchers strove to develop the electrochemical performance [3–5] and mechanical properties [6, 7] of batteries both experimentally and by simulation. The LIB mainly consists of a positive electrode, negative electrode, and separator, and the separator is set up between positive and negative electrodes to prevent internal short circuit [8, 9]. Because the potential of graphite is very close to that of lithium,

lithium dendrites are formed on the surface of the negative electrode when the battery is being charged. When separator suffers mechanical failure under external loading, the lithium dendrites may puncture the separator, which can lead to internal short circuit or explosion of LIB because of the direct contact of positive and negative electrodes [9]. The application field and safety of the battery is largely determined by the mechanical behavior of the separator. Therefore, high tensile strength and good toughness play an important role in improving the mechanical performances of the separator, such as resistance to external force, service life and so on.

*Corresponding author, e-mail: fhwang@nwpu.edu.cn
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The previous researches mainly focused on the essential properties of the separator, such as porosity, permeability [10], and thermal stability [11, 12]. The modification and fabrication processes of a separator with different materials [13–15] were also investigated. Because of the large variety of the fabrication processes, the mechanical properties of separator are different. The separator fabricated by dry process had obvious anisotropic performance along the machine direction (MD), diagonal direction (DD) and transverse direction (TD), but the separator fabricated by wet process had not. There were some testing standards to characterize the mechanical properties of a separator, such as American Society for Testing Materials (ASTM) D638 and D882 [12, 16] for tension, and ASTM D4830 [17] and D3763 [12, 16] for puncture resistance. In order to study the anisotropy effect, different types of separators were investigated by Zhang *et al.* [16], and the deformation and failure modes were studied. A series of experiments were designed by Xu *et al.* [18] to study the coupled effect of strain rate and environmental factor on the dynamic behavior of separator. The failure modes of two types of separators under uniaxial and biaxial loadings were investigated by Kalnaus and coworkers [17, 19, 20]. Therefore, the temperature, strain rate, and environmental factor (dry, water, and dimethyl carbonate) all affected the mechanical behaviors of separator [17, 18, 21].

The previous researches provide a solid foundation to understand the mechanical behavior of separator under external loading. However, there are a few pieces of research about the constitutive relation and micro-buckling behavior of separators in recent years. Therefore, the purpose of the present research is to investigate the anisotropy effect, strain rate effect, and micro-buckling behavior of separator. Based on anisotropy property, a numerical model is built to simulate the deformation of a separator. Furthermore, the strain rate-dependent constitutive relationship and a micro-buckling model are established. The research offers several highlights, such as (1) constitutive relationship with the strain rate effect of macromolecular separator is derived, based on the large deformation behavior; (2) parameters characterizing micro-buckling behavior are proposed and discussed; (3) the strain rate and anisotropy effects provide guidance to improve the manufacturing procedure, explore the mechanical property of macromolecular separator and address the safety issue of LIB.

2. Experimental and numerical models

2.1. Experimental model

In the present study, the experiments were performed on trilayer Celgard 2325 and Celgard H1612 separators, which were composed of polypropylene/polyethylene/polypropylene (PP/PE/PP). The materials of these separators were processed by dry stretching to create an open and straight porous structure [12, 22]. Microstructures of in-plane and cross-section views of separators were observed using an extra-high resolution field emission scanning electron microscope (FE-SEM, FEI Verios G4) in a vacuum environment with 10 and 2 kV accelerating voltages, as shown in Figure 1. The thickness, permeability, porosity, PP pore size, and shrinkage of separator are the important parameters to characterize the stability and long cycle life of LIB. The properties of Celgard 2325 and Celgard H1612 are summarized in Table 1 [12, 23, 24]. It is noted that the permeability of separators can be described by the MacMullin number. The MacMullin number is proportional to air permeability and it is often expressed by the JIS (Japanese Industrial Standards) Gurley value [12]. There is a certain degree of anisotropy in the separator due to its manufacturing procedure (submicron pore) and mechanical property (tensile strength) difference between MD and TD. The PP pores should be small enough to prevent the penetration of the electrode particles and conducting additives. The uniform distribution and tortuous structure of the PP pores contribute to the inhibition of lithium dendrites. Typically, the PP pore size ($<1\ \mu\text{m}$) is desirable for separators used in LIB. The porosity of the separator is defined by the weights of separator before and after the liquid absorption, i.e., $\text{Porosity} = [(\Omega - \Omega_0)/\rho_l V_0] \cdot 100\%$, where Ω_0 and Ω are the weights of separator before and after immersing the liquid, respectively, ρ_l is the density of the liquid, and V_0 is the geometric volume of the separator. The desirable porosity of normal LIB separator is about 40~60%. The thermal shrinkage ($<5\%$) at $90\ ^\circ\text{C}/1\ \text{h}$ is also determined by orthogonal directions.

According to ASTM D638 tension testing standard for a polymer material, the samples were prepared along MD, TD, and DD, as shown in Figure 2. To ensure the consistency of sample geometry, an acrylic template with 0.5 mm thickness was milled. Samples were cut along the perimeter of the acrylic template on transparent Cartesian graph paper to improve dimensional accuracy and cut quality. The total length

Figure 1. Microstructures of in-plane and cross-section views of (a) Celgard 2325 and (b) Celgard H1612 macromolecular separators.

Table 1. Properties of Celgard 2325 and Celgard H1612 [12, 23, 24].

Separators	Thickness [μm]	Permeability (JIS Gurley) [s]	Porosity [%]	PP pore size [μm]	Tensile strength [MPa]		Puncture strength [N]	Thermal stability (Shrinkage) 90 °C/1 h [%]	
					TD	MD		TD	MD
Celgard 2325 (PP/PE/PP)	25	620	39	0.028	14.71	166.71	>3.724	0	<5
Celgard H1612 (PP/PE/PP)	16	250	44	0.036	15.69	196.13	>3.528	0	<1.6

NOTE: (1) The uniformity of separator thickness plays an important role in the stable and long cycle life of LIB. Typically, separators used in rechargeable battery are 20~25 μm in thickness.
 (2) The permeability of separators can be described by the MacMullin number [12]. The MacMullin number is proportional to air permeability and it is often expressed by the JIS (Japanese Industrial Standards) Gurley value.
 (3) The PP pores should be small enough to prevent the penetration of the electrode particles and conducting additives. Typically, a submicron PP pore size (<1 μm) is desirable for separators used in LIB.
 (4) The separator porosity of separator is defined by the weights of separator before and after the liquid absorption. The desirable porosity of normal LIB separator is about 40~60%.
 (5) Separators must not shrink and wrinkle apparently when the temperature rises. The requirement of thermal shrinkage is generally less than 5% at 90 °C/1 h.

and width of samples were fixed at $L = 80$ mm and $B = 20$ mm. The gauge length was chosen as $l = 35$ mm. The two ends of the sample were glued with rubber to prevent sliding and tearing, and then they were held by two flat grips of testing machine

(Figure 2). The experiment was performed by SANS CMT4104 electronic universal testing machine with a 500 N load cell (0.005 N accuracy). All experiments were carried out at 30 °C under different strain rates.

Figure 2. Celgard 2325 and Celgard H1612 macromolecular separators [24] along machine direction (MD), transverse direction (TD) and diagonal direction (DD) (a). Prepared separator sample with rubber clamped ends (b). Tension experiment using the SANS CMT4104 electronic universal testing machine (c).

2.2. Numerical model

The numerical model was established by numerical code ABAQUS/explicit to investigate the tension deformation of anisotropic separators. The stress field of separator under uniaxial tension was approximated with a plane stress field ($\sigma_z = 0$ and $\tau_{xz} = \tau_{yz} = 0$) [25]. Because large plastic strain and anisotropy property existed in the research, the material properties of separator were different along MD, DD, and TD. The material properties (0° , 45° , and 90° materials) in ABAQUS were inputted according to the stress-strain curves in MD, DD, and TD of the experiment. The 4-node quadrilateral membrane, reduced integration, hourglass control element (M3D4R) was adopted and two integration points were used along the separator thickness. The numerical model comprised

17980 nodes and 17500 elements. One end of the numerical model was fixed and the other end was stretched under different strain rates.

3. Results and discussion

3.1. Anisotropy effect and deformation

The stress-strain curves of typical separator along MD under strain rate are shown in Figure 3a by repeating three identical samples to ensure accuracy and reliability. The three parallel experimental results are in good consistency, and stress-strain curves are divided into five phases. The elastic phase consists of an initial linear elastic phase (phase I) and nonlinear elastic phase (phase II). The elasticity modulus is obtained by the slope of phase I. The nonlinearity effect, and elastic enhancement effect are displayed

clearly after strain reaches 0.1 during the elastic phase. The plastic phase consists of yield phase (phase III) and cold drawing phase (phase IV). During the cold drawing phase, the random orientated

Figure 3. Mechanical properties of Celgard 2325 under uniaxial tension. (a) Repeatability ($\dot{\epsilon} = 0.005 \text{ s}^{-1}$), anisotropy effect ($\dot{\epsilon} = 0.005 \text{ s}^{-1}$) and failure modes ($\dot{\epsilon} = 0.05 \text{ s}^{-1}$ and $\dot{\epsilon} = 0.005 \text{ s}^{-1}$) of separators along MD, DD and TD. (b) Comparison of numerical and experimental results along MD, DD and TD.

amorphous polymer of the separator is transformed into an ordered amorphous polymer. So cold drawing plays an important role in improving the strength and surface state of the separator. The last phase is the failure phase (phase V). The separator along MD shows obvious elastic behavior, and it has no strain hardening effect. The anisotropy effect along MD, DD, and TD are observed remarkably in Figure 3a. The strain hardening effect is displayed along DD and TD after strain reaches 0.28 and 0.07, respectively. The elasticity moduli along MD, DD, and TD are $E_{MD} = 554$ MPa, $E_{DD} = 363$ MPa, and $E_{TD} = 206$ MPa, the failure stresses are $\sigma_{fMD} = 158$ MPa, $\sigma_{fDD} = 19.2$ MPa and $\sigma_{fTD} = 12.2$ MPa, and corresponding failure strains are $\epsilon_{fMD} = 0.97$, $\epsilon_{fDD} = 7.8$, and $\epsilon_{fTD} = 14.4$, respectively. Therefore, the separator along MD has higher strength but lower toughness compared with that along DD and TD.

Because there is a large anisotropy effect in the separator, the deformation and failure modes along different directions are quite different. The deformation and failure modes of Celgard 2325 along MD, TD, and DD are shown in Figure 3a. The failure cross-section presents a zigzag pattern along MD while it is much smoother along TD. Because the mechanical strength is the same for given cross-section, the fracture direction is vertical to the corresponding loading direction, and this fracture is mainly caused by tensile failure. However, there is a certain angle [16] between the loading direction and the fracture direction along DD, as shown in Figure 3a. The main reason for this rotation phenomenon is that the mechanical strength on both sides of a given cross-section is different and this fracture is mainly caused by tensile and shear failures. Also, the failure strain of separator along MD ($\epsilon_{fMD} = 0.97$) is much less than that along TD ($\epsilon_{fTD} = 14.4$) and DD ($\epsilon_{fDD} = 7.8$, $\dot{\epsilon} = 0.005$ s⁻¹).

Because the deformation modes of Celgard H1612 in numerical results are similar to those of Celgard 2325, only the comparisons of numerical results and experimental results of Celgard 2325 along MD, DD, and TD are shown in Figure 3b. Because calculation with excessive deformation may not converge, the finite deformation is considered in the numerical model. The numerical results are in good agreement with experimental results. The rotation phenomenon along DD is observed in numerical and experimental results (Figure 3b). The strain-softening is not displayed in separator along MD due to high fracture

strength and low fracture toughness, while it is obviously displayed along TD because of low fracture strength and high fracture toughness. Besides, the strain-softening degree of the separator along DD is between the above two cases.

3.2. Strain rate effect

As shown in Figure 3a, an obvious strain rate effect of separator is observed (failure strain $\epsilon_{fDD} = 4.6$ when the strain rate $\dot{\epsilon} = 0.05$ s⁻¹ is less than $\epsilon_{fDD} = 7.8$ when strain rate $\dot{\epsilon} = 0.005$ s⁻¹). Therefore, the stress-strain curves of Celgard 2325 and Celgard H1612 along MD, DD and TD under three strain rates (0.002 s⁻¹, 0.02 s⁻¹ and 0.2 s⁻¹) are investigated systematically (Figure 4). It can be seen that strain neutrality along MD (Figure 4a) and strain hardening along DD (Figure 4b) and TD (Figure 4c) are displayed in the cold drawing phase. The results show that with the increment of strain rate, the elastic modulus, and yield stress increase while the failure strain decreases. Additionally, the Celgard 2325 has higher failure strain compared with Celgard H1612 in the same strain rate.

The nonlinearity and strain hardening/softening/neutrality effects are displayed obviously in the cold drawing phase, and the degree of nonlinearity depends on the strain rate of the separator (Figure 4). It is assumed that the total strain of separator is the sum of an elastic strain term and an inelastic strain term [26–28], see Equation (1):

$$\epsilon = \epsilon_e + \epsilon_i \quad (1)$$

where ϵ_e and ϵ_i are the elastic strain and inelastic strain, respectively. The elastic strain induced by loading is independent of loading history and path. The constitutive relation of separator obeys Hooke's law in the elastic phase. The elastic strain is written by Equation (2):

$$\epsilon_e = \frac{\sigma}{E(\dot{\epsilon})} \quad (2)$$

where $E(\dot{\epsilon})$ is the function of the strain rate. It is assumed that the constitutive relation of separator obeys power law in inelastic phase. Therefore Equation (3):

$$\epsilon_i = J(\dot{\epsilon})\sigma\epsilon^\kappa \quad (3)$$

where $J(\dot{\epsilon}) = 1/E(\dot{\epsilon})$ is tension compliance constant, which is the function of strain rate, and κ is the power exponent. Introducing Equations (2) and (3)

Figure 4. Stress-strain curves of Celgard 2325 and Celgard H1612 along different tension directions under three strain rates (0.002 s^{-1} , 0.02 s^{-1} and 0.2 s^{-1}). (a) MD. (b) DD. (c) TD.

into Equation (1), the constitutive equation can be written by Equation (4):

$$\sigma = \frac{E(\dot{\epsilon})\epsilon}{1 + E(\dot{\epsilon})J(\dot{\epsilon})\epsilon^{\kappa}} \quad (4)$$

The strain hardening/softening/neutrality of separator is determined by the slope of the stress-strain curve in Equation (A.3). The slope of the stress-strain curve is discussed in Appendix A.1. The effects of power

exponent κ and tension compliance J on the stress of separator are shown in Appendix A.1.

According to Johnson-Cook theory, many researchers [29–31] have established the strength logarithmic functions to measure strain rate effect of composite material. The elastic modulus $E(\dot{\epsilon})$ and yield stress $\sigma_s(\dot{\epsilon})$ which considering strain rate-dependent [29, 31] can be described by Equations (5) and (6):

$$E(\dot{\epsilon}) = E_0 \left(1 + \lambda_1 \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right) \quad (5)$$

$$\sigma_s(\dot{\epsilon}) = \sigma_{s0} \left(1 + \lambda_2 \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right) \quad (6)$$

where E_0 , σ_{s0} and $\dot{\epsilon}_0$ are reference elastic modulus, reference yield stress, and reference plastic strain rate, respectively. $\dot{\epsilon}$ is the actual strain rate component, λ_1 and λ_2 are defined as strain rate strengthening coefficients in Equation (5) and Equation (6), and the expressions are $\lambda_1 = \partial E(\dot{\epsilon}) / (E_0 \partial \ln \dot{\epsilon})$, $\lambda_2 = \partial \sigma_s(\dot{\epsilon}) / (\sigma_{s0} \partial \ln \dot{\epsilon})$, $\dot{\epsilon}_0 = 0.002 \text{ s}^{-1}$.

The power exponent κ and strain rate strengthening coefficient λ_1 are determined by introducing Equation (5) and $J(\dot{\epsilon}) = 1/E(\dot{\epsilon})$ into Equation (4), the constitutive equation can be written as Equation (7):

$$\ln \left\{ \frac{\epsilon}{\sigma} - \frac{1}{E_0 [1 + \lambda_1 (\ln \dot{\epsilon} - \ln \dot{\epsilon}_0)]} \right\} = \kappa \ln \epsilon - \ln E_0 - \ln [1 + \lambda_1 (\ln \dot{\epsilon} - \ln \dot{\epsilon}_0)] \quad (7)$$

Besides, the yield stress σ_s and yield strain ϵ_s are given by Equations (A.4) and (A.5). The strain rate-dependent relationship among power exponent κ , strain rate strengthening coefficients λ_1 and λ_2 are determined by introducing Equation (A.4), (A.5) and $J(\dot{\epsilon}) = 1/E(\dot{\epsilon})$ into Equation (6), i.e. Equation (8):

$$\ln \left(\frac{\sigma_{s0}}{E_0} \right) = \frac{\kappa - 1}{\kappa} \ln(\kappa - 1) - \ln \kappa + \ln \left(\frac{1 + \lambda_1 (\ln \dot{\epsilon} - \ln \dot{\epsilon}_0)}{1 + \lambda_2 (\ln \dot{\epsilon} - \ln \dot{\epsilon}_0)} \right) \quad (8)$$

The strain rate-dependent material parameters of two separators along MD, DD, and TD, i.e. elastic modulus E and yield stress σ_s , are derived from stress-strain curves, respectively, as shown in Figure 5a, 5b. It can be seen that these linear curves are nearly parallel to each other at the same tension direction and strain rate. It means that strain rate strengthening coefficients λ_1 and λ_2 about elastic modulus and yield stress of different separators are the same, respectively. Microstructures of Celgard 2325 and Celgard H1612 along TD under 0.02 s^{-1} are shown in Figure 5c. The strain rate strengthening coefficients of two separators along MD, DD, and TD are listed in Table 2. The elastic modulus and yield stress of Celgard H1612 are greater than that of Celgard 2325, respectively. The maximum errors of strain

Table 2. Strain rate strengthening coefficient of Celgard 2325 and Celgard H1612 along MD, DD, and TD.

Tension direction	Material parameter	Celgard 2325	Celgard H1612	Errors
MD	E_0 [MPa]	460.66	505.47	—
	λ_1	$2.24 \cdot 10^{-1}$	$2.16 \cdot 10^{-1}$	3.57%
	σ_{s0} [MPa]	149.49	160.78	—
	λ_2	$4.87 \cdot 10^{-2}$	$4.85 \cdot 10^{-2}$	0.41%
DD	E_0 [MPa]	276.40	342.37	—
	λ_1	$3.11 \cdot 10^{-1}$	$2.80 \cdot 10^{-1}$	9.97%
	σ_{s0} [MPa]	15.06	14.81	—
	λ_2	$4.89 \cdot 10^{-2}$	$4.85 \cdot 10^{-2}$	0.82%
TD	E_0 [MPa]	165.21	205.18	—
	λ_1	$3.41 \cdot 10^{-1}$	$3.07 \cdot 10^{-1}$	9.97%
	σ_{s0} [MPa]	10.04	9.91	—
	λ_2	$3.56 \cdot 10^{-2}$	$4.18 \cdot 10^{-2}$	14.83%

rate strengthening coefficients λ_1 and λ_2 about material parameters are less than 15%.

3.3. Micro-buckling behavior

A series of micro-buckling modes and crazing phenomenon of separator are observed in the x - and y -directions during tension experiment, as shown in Figure 6a. The main reason is that a certain range of tension strains exist since the limit of clamped boundary condition [32]. When the separator is subjected to a constant tensile force, strength redistribution along tension direction exists because polymer molecules may be preferentially aligned in the cold drawing phase [33]. For the separator loaded by tension force per unit length, according to Equations (B.4) and (B.5) in Appendix B, the buckling partial differential equilibrium equation of separator can be stated by Equation (9):

$$D \left(\frac{\partial^4 w}{\partial x^4} + 2 \frac{\partial^4 w}{\partial x^2 \partial y^2} + \frac{\partial^4 w}{\partial y^4} \right) = F_x \frac{\partial^2 w}{\partial x^2} + F_y \frac{\partial^2 w}{\partial y^2} \quad (9)$$

The deflection $w(x,y)$ in z -direction for any given point $\zeta(x,y)$ can be assumed as double harmonic function, as shown by Equation (10):

$$w(x,y) = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_{nm} \sin \frac{n\pi x}{l} \sin \frac{m\pi y}{B} \quad (10)$$

where n and m are the half-wave numbers in x - and y -directions, respectively. It may be noted that the double harmonic function automatically satisfies boundary conditions, that is $w = 0$ at $x = 0$, $x = l$ and $y = 0$, $y = B$.

According to Equation (B.7), the tension force in the x -direction of the separator is given by Equation (11):

Figure 5. (a) Strain rate-dependent elastic modulus and yield stress of Celgard 2325. (b) Strain rate-dependent elastic modulus and yield stress of Celgard H1612. (c) Microstructures of Celgard 2325 and Celgard H1612 along TD under strain rate 0.02 s^{-1} .

$$F_x = -\frac{\pi^2 E t^3}{12(1-\mu^2)} \frac{\left[\left(\frac{n}{l}\right)^2 + \left(\frac{m}{B}\right)^2\right]^2}{C\left(\frac{m}{B}\right)^2 + \left(\frac{n}{l}\right)^2} \quad (11)$$

where $C = F_y/F_x = \sigma_y l / \sigma_x B \leq 0$ is the proportionality factor. For tension experiment, the direction of mid-plane internal force F_x and F_y is opposite according to Poisson effect [32]. Based on Equation (11), the critical stress-causing buckling in the x -direction of the separator is written by Equation (12):

$$\sigma_{x,\text{crit}} = -\frac{\pi^2 E}{12(1-\mu^2)} \left(\frac{t}{B}\right)^2 \frac{[m^2 + (nB/l)^2]^2}{Cm^2 + (nB/l)^2} \quad (12)$$

We set $k = [m^2 + (nB/l)^2] / [Cm^2 + (nB/l)^2]$ as the Euler's buckling coefficient. When $F_x \gg F_y$, $C = 0$,

$m = 1$, buckling coefficient k is reduced to $k = (l/nB + nB/l)^2$ which is presented by Bulson [34]. The minimum half-wave number $n_{\min}$ is determined by stationary condition $\partial k / \partial n = 0$, so $n_{\min} = ml\sqrt{1 - 2C/B}$. So the minimum buckling coefficient and the critical stress in the x -direction are given by Equations (13) and (14):

$$k_{\min} = 4(1 - C) \quad (13)$$

$$\sigma_{x,\text{crit}} = -\frac{\pi^2 E (1 - C)}{3(1 - \mu^2)} \left(\frac{t}{B}\right)^2 \quad (14)$$

The minimum enveloping curves of buckling coefficient can be found from the change of half-wave numbers of separator with different length-width

Figure 6. Micro-buckling behaviors of macromolecular separators. (a) Tension experimental result of Celgard 2325 along TD, and micro-buckling mode of simulation result. (b) Enveloping curves about the change of buckling coefficient with half-wave numbers of separator with different length-width ratios. (c) Critical stress changes with proportionality factor in the x -direction.

ratios, as shown in Figure 6b. The changes of critical stress in the x -direction of separator for different m and n are shown in Figure 6c. The change curves of critical stress are divided into two regions: tensile stress (positive value) and compressive stress (negative value). The maximum tensile stress increases and maximum compressive stress decreases with the increment of half-wave number m , as shown in Figure 6c. The half-wave number m obviously determines the failure mode of separator. For example, failure stress is compressive stress when $m = 3$, while it is tensile stress when $m = 8$. Therefore the failure region of separator is situated near compressive stress region for every micro-buckling element due to $m = 5$. In addition, the maximum tension and compressive stresses increase with half-wave number n , as shown in Figure 6c. The tensile stress is approximately equal to maximum compressive stress. The result shows that the effect of half-wave number n on a failure mode is not obvious in a certain stress ratio range. To determine critical stress in the x -direction $\sigma_{x,crit}^*$, a simple expression is proposed by introducing coefficient k_c [32, 35]. So the critical stress is $\sigma_{x,crit}^* = k_c E(t/B)^2$, where $k_c = -k\pi^2/12(1 - \mu^2)$ and k_c is acquired by numerical diagram [32]. The critical stresses in the x -direction of Celgard 2325 and Celgard H1612 along TD are equal to $\sigma_{crit,2325} = 12.5$ MPa, and $\sigma_{crit,1612} = 13.1$ MPa respectively, the error rates are approximately $Error = 2.5\%$ and $Error = 6.9\%$ compared with experimental results.

4. Conclusions

The strain rate effects and micro-buckling behaviors of Celgard 2325 and Celgard H1612 anisotropic separators under uniaxial tension are investigated for LIB. The results conclude that the anisotropy effect and strain rate effect of separator along MD, DD, and TD are displayed obviously. A typical stress-strain curve is divided into five phases: elastic phase, nonlinear elastic phase, yield phase, cold drawing phase, and failure phase. The separator along MD has higher strength but lower toughness compared with that along DD and TD. In addition, the mesh rotation phenomenon along DD is observed in numerical and experimental results. Finally, with the increment of strain rate, the elastic modulus, and yield stress increase while the failure strain decreases. The strain neutrality along MD and strain hardening along DD and TD are displayed in the cold drawing phase. The Celgard 2325 has higher failure strain

compared with Celgard H1612 in the same strain rate. The strain rate-dependent constitutive relationship among power exponent, strain rate strengthening coefficients is $\ln\{\varepsilon/\sigma - 1/E_0[1 + \lambda_1(\ln\dot{\varepsilon} - \ln\dot{\varepsilon}_0)]\} = \kappa \ln\varepsilon - \ln E_0 - \ln[1 + \lambda_1(\ln\dot{\varepsilon} - \ln\dot{\varepsilon}_0)]$. The maximum error of strain rate strengthening coefficient $\lambda_1 = \partial E(\dot{\varepsilon})/(E_0 \ln(\dot{\varepsilon}))$ and $\lambda_2 = \partial \sigma_s(\dot{\varepsilon})/(\sigma_{s0} \ln(\dot{\varepsilon}))$ about the material parameter is less than 15%. The critical stresses in the x -direction $\sigma_{x,crit} = -Ek\pi^2(t/B)^2/12(1 - \mu^2)$ of Celgard 2325 and Celgard H1612 along TD are 12.5 Pa and 13.1 MPa respectively, and the error rates are $Error = 2.5\%$ and 6.9% compared with the experimental result. The above investigation provides guidance for improving the manufacturing procedure, exploring the mechanical property of macromolecular separator and addressing the safety issue of LIB.

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Appendix A.

Slope of the stress-strain curve, yield stress and yield strain

A.1. Slope of the stress-strain curve

According to Equation (4), the slope of the stress-strain curve is the derivative of stress σ with respect to ε , that is Equation (A.1):

$$\frac{\partial \sigma}{\partial \varepsilon} = \frac{E(\dot{\varepsilon})[1 + (1 - \kappa)E(\dot{\varepsilon})J(\dot{\varepsilon})\varepsilon^\kappa]}{[1 + E(\dot{\varepsilon})J(\dot{\varepsilon})\varepsilon^\kappa]^2} \quad (A.1)$$

For elastic material with small strain, the total strain satisfies condition $\varepsilon^\kappa \ll 1$; For plastic material with large strain, the total strain satisfies the condition $\varepsilon^\kappa \gg 1$. Equation (A.1) can be simplified as Equation (A.2):

$$\frac{\partial \sigma}{\partial \varepsilon} = \begin{cases} E(\dot{\varepsilon}) & (\varepsilon^\kappa \ll 1) \\ \frac{1 - \kappa}{J(\dot{\varepsilon})\varepsilon^\kappa} & (\varepsilon^\kappa \gg 1) \end{cases} \quad (A.2)$$

For plastic material with small strain, i.e. $\varepsilon^\kappa \ll 1$, the material is in the elastic stage and the elastic modulus $E = d\sigma/d\varepsilon$. For plastic material with large strain, i.e. $\varepsilon^\kappa \gg 1$, the post-yield behavior includes strain hardening ($\partial\sigma/\partial\varepsilon > 0$), strain softening ($\partial\sigma/\partial\varepsilon < 0$),

Figure 7. Stress-strain curves of separator: (a) the effect of power exponent κ on stress; (b) the effect of tension compliance J on stress.

and strain neutrality ($\partial\sigma/\partial\varepsilon = 0$). For plastic material with large strain in Equation (A.2), Equation (4) can be reduced as Equation (A.3):

$$\sigma = \begin{cases} \frac{1}{J(\dot{\varepsilon})} \varepsilon^{1-\kappa} & (\kappa < 1) \text{ strain hardening} \\ \frac{1}{J(\dot{\varepsilon})} & (\kappa = 1) \text{ strain neutrality} \\ \frac{1}{J(\dot{\varepsilon})} \varepsilon^{1-\kappa} & (\kappa > 1) \text{ strain softening} \end{cases} \quad (\text{A.3})$$

The post-yield behavior of separator is strain hardening when $\kappa < 1$, strain-softening when $\kappa > 1$ and strain neutrality when $\kappa = 1$. The stress-strain curves of separator change with power exponent κ , as shown in Figure 7a. The power exponent affects not only the shape of stress-strain curves but also the stress values. The post-yield behaviors of separator are determined by power exponent. The simplified material behaviors, including elastic linear softening, elastic perfectly plastic and elastic linear hardening, are also given in Figure 7a. The stress values increase with increasing power exponent κ . The stress-strain curves of separator change with tension compliance J , as shown in Figure 7b. The stress values increase with decreasing tension compliance J .

A.2. Yield stress and yield strain

The yield stress σ_s and yield strain ε_s are determined by the slope of the stress-strain curve, i.e. $\partial\sigma/\partial\varepsilon = 0$ when $\sigma = \sigma_s$ and $\varepsilon = \varepsilon_s$. According to Equation (A.1), the yield strain ε_s is Equation (A.4):

$$\varepsilon_s = \left[\frac{1}{(\kappa - 1)E(\dot{\varepsilon})J(\dot{\varepsilon})} \right] \quad (\text{A.4})$$

Introducing Equations (A.4) and (5) into Equation (4), the yield stress σ_s can be written by Equations (A.5):

$$\sigma_s = \frac{(\kappa - 1)^{1-1/\kappa}}{\kappa} E_0 [1 + \lambda_1 (\ln \dot{\varepsilon} - \ln \dot{\varepsilon}_0)] \quad (\text{A.5})$$

Appendix B.

Derivation of buckling partial differential equilibrium equation

The infinitesimal element of separator under internal bending force and mid-plane internal force is shown in Figure 8. The equilibrium condition of internal force along z -direction is obtained by Figure 8b as Equations (B.1):

$$\sum z = 0: \quad \frac{\partial Q_x}{\partial x} + \frac{\partial Q_y}{\partial y} + F_x \frac{\partial^2 w}{\partial x^2} + F_y \frac{\partial^2 w}{\partial y^2} = 0 \quad (\text{B.1})$$

where $w(x,y)$ is the deflection in z direction for any given point $\zeta(x,y)$, and F_x, F_y are uniformly tension force in x -direction and compression force in y -direction, respectively.

The equilibrium condition of the moment is obtained along x' - and y' - directions (which are parallel to x - and y -directions respectively) by Figure 8a as Equations (B.2) and (B.3):

$$\sum M_{x'} = 0: \quad \frac{\partial M_y}{\partial y} + \frac{\partial M_{xy}}{\partial x} = Q_y \quad (\text{B.2})$$

$$\sum M_{y'} = 0: \quad \frac{\partial M_x}{\partial x} + \frac{\partial M_{xy}}{\partial y} = Q_x \quad (\text{B.3})$$

Figure 8. Infinitesimal element of separator under combined force: (a) internal bending force; (b) mid-plane internal force.

Substituting Equations (B.2) and (B.3) in Equation (B.1), the equilibrium condition is Equation (B.4):

$$\frac{\partial^2 M_x}{\partial x^2} + 2 \frac{\partial^2 M_{xy}}{\partial x \partial y} + \frac{\partial^2 M_y}{\partial y^2} + F_x \frac{\partial^2 w}{\partial x^2} + F_y \frac{\partial^2 w}{\partial y^2} = 0 \quad (\text{B.4})$$

The edge bending moments M_x , M_y and twisting moment M_{xy} per unit length [34, 35] on a separator element is Equation (B.5):

$$\begin{cases} M_x = -D \left(\frac{\partial^2 w}{\partial x^2} + \mu \frac{\partial^2 w}{\partial y^2} \right) \\ M_y = -D \left(\frac{\partial^2 w}{\partial y^2} + \mu \frac{\partial^2 w}{\partial x^2} \right) \\ M_{xy} = -D(1 - \mu) \frac{\partial^2 w}{\partial x \partial y} \end{cases} \quad (\text{B.5})$$

where $D = Et^3/(12(1 - \mu^2))$ is the bending stiffness of separator, and t is the thickness of separator element.

Inserting Equation (10) into Equation (9), the equilibrium equation is given by Equation (B.6):

$$D \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} A_{nm} \left(\left(\frac{n\pi}{l} \right)^2 + \left(\frac{m\pi}{B} \right)^2 \right)^2 + F_x \left(\frac{n\pi}{l} \right)^2 + F_y \left(\frac{m\pi}{B} \right)^2 \cdot \sin \frac{n\pi x}{l} \sin \frac{m\pi y}{B} = 0 \quad (\text{B.6})$$

For Equation (B.6), $w = 0$ when $A_{nm} = 0$ and microbuckling of the separator does not happen. So $w \neq 0$ when $A_{nm} \neq 0$. According to Equation (B.6), the equilibrium equation is given by Equation (B.7):

$$D \left(\left(\frac{n\pi}{l} \right)^4 + 2 \left(\frac{n\pi}{l} \right)^2 \left(\frac{m\pi}{B} \right)^2 + \left(\frac{m\pi}{B} \right)^4 \right) = -F_x \left(\frac{n\pi}{l} \right)^2 - F_y \left(\frac{m\pi}{B} \right)^2 \quad (\text{B.7})$$

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