

Effect of polymer blending and drawing conditions on properties of polyethylene separator prepared for Li-ion secondary battery

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Abstract

A separator made of the polymer blends of high density polyethylene (HDPE) and ultra-high molecular weight polyethylene (UHMWPE) is prepared by a wet process for the Li-ion secondary battery. An investigation is made of the effect on the mechanical properties of the separator by the blending of the polymers and the drawing conditions. The mechanical strength is increased with increasing molecular weight and content of UHMWPE polymer. A film containing 6 wt.% UHMWPE has a tensile strength of about 1000 kg cm⁻² at a draw ratio of 5. The pores of the separator are very uniform with a size of 0.1–0.12 μm. The shut-down (SD) characteristics increase rapidly in the vicinity of 130 °C and the fusion temperature is 160 °C. These features suggest that the separator is applicable to the Li-ion secondary battery. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In 1991, Sony successfully launched the first commercial Li-ion battery. This heralded the start of a new generation of rechargeable batteries, which will eventually overtake the present generation of nickel–cadmium and nickel–metal hydride batteries. The demand for batteries of high capacity has increased with the proliferation of electronic equipment, portable computers, and cellular phones. As the demand for higher-power, longer-lasting batteries is increasing dramatically, more and more companies are beginning to produce Li-ion batteries and the technology is attracting considerable research and development effort.

Li-ion batteries are constructed by using a lithium oxide positive electrode (cathode) and a carbon negative electrode (anode) with a high polymer separator and a non-aqueous electrolyte. The Li-ion battery is expected to be a power source of a large capacity. The average discharge voltage is 3.6 V, the energy density is 300 Wh dm⁻³, and the specific energy is 120–140 Wh kg⁻¹. The energy density and specific energy are higher than that of nickel–cadmium, which has values of 90–160 Wh/dm³ and 50–70 Wh kg⁻¹, respectively.

Compared with nickel–cadmium, Li-ion batteries also exhibit longer cycle life (more than 1000–1200 cycles) and minimal self-discharge (<10% per month).

The main objection to rechargeable lithium batteries is based on safety considerations. Redeposited lithium is far more active than the metal itself and there is the possibility of side-reactions or thermal run-away when short-circuits are formed. This problem is resolved by using Li-ion rather than lithium metal. Positive temperature coefficient (PTC) elements and fuses also protect Li-ion secondary batteries from overcurrent as well as from overcharge (overvoltage). A PTC device is used for external short-circuit protection. An excessive voltage triggers electric current that heats up elements in the device to melt the fuse, and thus protects the circuit.

Placed between the cathode and anode, the separator is required to function as an electric insulator and retain a large quantity of electrolytic solution, while maintaining high ion permeation and low electrical resistance [1]. It is also required to be chemically stable against electrolytic solutions, electrochemically stable, and sufficiently mechanically strong to withstand the assembly process. For use in lithium batteries, it must provide certain meltdown characteristics. That is, if the battery is extremely short-circuited for some reason, thus causing the internal temperature to reach the melting point of the separator material, then the separator must melt down, fill the hole and suspend the flow

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of electric current so that the battery reactions are suppressed and heat generation is halted in order to insure safety. This safety mechanism, based on meltdown of the separator, provides the only means of ensuring safety in cases where safety elements such as PTC and fuses do not function.

In most batteries, the separators are made of non-woven fabrics or minute polymeric films. The materials used in non-woven fabrics include a single polyolefin, or a combination of polyolefins, such as polyethylene (PE) and polypropylene (PP); polyamide (PA), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF); and polyvinyl chloride (PVC). Usually, the fabrics are made by adhering or hot-welding fabrics together. Because the fabric material, length, diameter and other characteristics influence the performance of the separator, each battery has a combination of fabrics that is best-suited for its function. Non-woven fabrics have not, however, been able to compete with microporous films. This is most probably because of the difficulty in making thin (25 μm) non-woven fabrics with acceptable physical properties.

Currently, all commercially available, spirally wound, Li-ion cells use microporous polyolefin separators such as PE and PP. They are selected because they provide films with uniform pore size. The PE separator, which melts down at 120–130 $^{\circ}\text{C}$, is expected to provide greater safety than the PP separator, which has a fuse temperature of 165 $^{\circ}\text{C}$. For use as separators in lithium batteries, however, not only the fuse temperature must be low but also the short-circuit temperature must be higher. From this perspective, there are moves towards solving this problem by developing composite films instead of a single-material film. Recently, a single-layer separator made from a PE/PE blend [2] or a PE/PP blend [3] has been patented. Tohnen, Asahi-Kasei, and Hoechst have patented a double-layer structure of PE/PP or a tri-layer structure of PP/PE/PP microporous membranes [4]. A tri-layer structure of PP/PE/PP microporous membranes provided exceptional puncture strength. In addition, the low melting PE layer (135 $^{\circ}\text{C}$) can act as a thermal fuse, while the higher-melting PP (165 $^{\circ}\text{C}$) layers provide physical integrity [5]. The fuse layer melts and loses porosity at elevated temperature, which effectively stops current flow between electrodes; the other layers do not melt and continue to provide mechanical integrity after the fuse layer has melted.

The methods for manufacturing microporous membranes can be broadly divided into wet processes [6] and dry processes [7]. Both processes usually employ one or more

orientation steps to impart porosity and/or increase tensile strength. The dry process involves no solvent handling, and is therefore inherently simpler than the wet process. Separators made by the dry process are available from Hoechst Celanese [8] and Nitto Denko [9]. Separators made by the wet process are available from Tonen [3,10] and Asahi-Kasei [11]. The wet process involves mixing a hydrocarbon liquid or some other low molecular weight substance with a polyolefin resin, heating and melting the mixture, extruding the melt into a sheet, orientating the sheet either in the machine direction or biaxially, and then extracting the liquid with a volatile solvent [7]. The dry process involves melting a polyolefin resin, extruding it into a film, thermal annealing, orientation at a low temperature to form micropore initiators, and then orientation at a high temperature to form micropores. In the present work, a single-layer separator has been prepared from a high density polyethylene (HDPE)/ultra-high molecular weight polyethylene (UHMWPE) blend by the wet process and the effect of drawing conditions on the mechanical properties of the separator has been studied.

2. Experimental

A polyolefin composition solution, as shown in Table 1, was prepared from a resin material which consisted of HDPE (manufactured by Samsung general chemical), UHMWPE (manufactured by Mitsui chemical) with an average molecular weight (M_w) of 2 400 000, UHMWPE (manufactured by Mitsui chemical) with an average molecular weight of 3 400 000, and paraffin oil (Teric, manufactured by ICI). An antioxidant (Irganox 1010, manufactured by Ciba Specialty Chemical) was added to the resulting PE composition solution to protect it from degradation by oxidation. The mixture was introduced into an autoclave which was equipped with a stirrer that had a double helical impeller. The mixture was stirred at 180 $^{\circ}\text{C}$ for 2 h to give a uniform solution. Next, a heated solution was extruded through a T-die into a sheet. The sheet was subjected to biaxial orientation by a biaxial stretching machine at 125–130 $^{\circ}\text{C}$ at a draw speed of 10–40 mm s^{-1} and at a draw ratio of 2:5. The resulting oriented membrane was washed with methylene chloride to remove the residual liquid paraffin, and then dried. The process produced a microporous membrane of a PE composition with a thickness of 25 μm . The thickness of the original undrawn membrane varied on the draw ratio used for the

Table 1
Polymer composition of samples for separator manufacturing

Sample	Blending conditions				
	HDPE	UHMWPE (M_w 2 400 000)	UHMWPE (M_w 3 400 000)	Oil (Teric)	Additive (Irganox 1010)
1	27	3		70	0.15
2	27	1.5	1.5	70	0.15
3	27		3	70	0.15
4	24	2	4	95	0.15

biaxial stretching. For example, if the linear draw ratio in the machine direction is five-fold, the areal draw ratio is 25-fold. The thickness of the original membrane was 625 μm to achieve a final thickness of 25 μm . The thickness of the membrane may vary depending on its application, but it is generally 25 μm .

The mechanical strength was measured by means of an Instron 4201 tester according to the ASTM D 822 procedure. The pore structure was measured by scanning electron microscopy (SEM Jeol JSM 840) and an Automatic Perm-porometer (Porous Materials Inc., APP2100E). Thermal properties were examined with differential scanning calorimetry (DSC Perkin-Elmer DSC7). The mechanical strength of a separator is characterized in terms of tensile properties and puncture strength. The tensile properties are dependent on the manufacturing processes. Uniaxially oriented films have high strength in only one direction, whereas biaxially oriented films are strong in both the machine and the transverse directions. Although, intuitively it might be expected that biaxially oriented films are to be preferred over uniaxially oriented films, in practice biaxial orientation provides no advantage. The separator must have sufficient strength in the machine direction so that it does not break under the stress of winding. The strength in the transverse direction is not so important as that in the machine direction during the process of making spirally-wound batteries. The minimum requirement for the mechanical strength of the separator is 1000 kg mm^{-2} for a membrane of 25 μm thickness.

Puncture strength has been used to indicate the tendency of separators to allow short-circuits in a cell that may occur due to holes generated in the separator by the rough surface of the cell during the charge–discharge cycle. Measurements of puncture strength are made with the tensile tester by measuring the weight required on a given needle to puncture a given separator [4].

The ac resistance of the porous film at 1 kHz was measured with a standard resistance meter. Resistance values were obtained according to the following equation [9]:

$$R = S(R_1 - R_0) \quad (1)$$

where R_0 is the resistivity (Ω) of the electrolytic solution; R_1 the resistivity (Ω) of a porous film soaked in electrolyte solution; S the sectional area (cm^2) of the porous film. The electrolyte used was LiPF_6 in propylene carbonate (PC). The resistance of the separator in this electrolyte solution was measured on heating to a temperature of 25–180 $^\circ\text{C}$ at a rate of 2 $^\circ\text{C}/\text{min}$ [9].

3. Results and discussion

A microporous separator is made by a wet process which involves mixing, extrusion, stretching, and extraction. The battery separator technology to manufacture this microporous membrane requires an optimization of the properties by mixing a high polymer with oil, forming

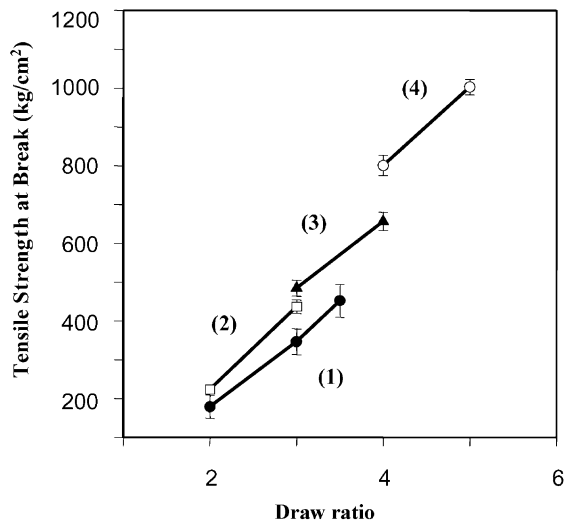


Fig. 1. Mechanical strength of separator according to polymer blending and extension conditions. (1) sample 1 HDPE (27 wt.%) / UHMWPE ($M_w = 240\,000\,000$, 3 wt.%); (2) sample 2 HDPE (27 wt.%) / UHMWPE ($M_w = 240\,000\,000$, 1.5 wt.%) / UHMWPE ($M_w = 340\,000\,000$, 1.5 wt.%); (3) sample 3 HDPE (27 wt.%) / UHMWPE ($M_w = 340\,000\,000$, 3 wt.%); (4) sample 4 HDPE (24 wt.%) / UHMWPE ($M_w = 240\,000\,000$, 2 wt.%) / UHMWPE ($M_w = 340\,000\,000$, 4 wt.%).

pores by phase separation, and stretching to obtain the necessary mechanical strength. The mechanical strength and pore structure are considered to be the most important properties of the separator. The mechanical strength of the separator as a function of polymer composition and draw-ratio is shown in Fig. 1. As is shown in Table 1, a series of microporous polyolefin membranes has been made from of a polyolefin composition solution prepared from a resin material which consisted of HDPE, UHMWPE ($M_w = 2\,400\,000$), and UHMWPE ($M_w = 3\,400\,000$). The polyolefin composition of the samples is varied such that the wt.% of samples 1, 2, 3, and 4 is 27:3:0, 27:1.5:1.5 and 24:2:4, respectively.

In fact, adding more than 4 wt.% UHMWPE to prepare a high concentration polyolefin solution was detrimental to processing due to a sudden increase in the viscosity of the solution. Theoretically, the upper limit in concentration to prepare a PE solution is determined by the molecular weight of the resin material. The concentration limits are 3 and 1% for a resin material which has a M_w of 8×10^5 and 1.5×10^5 , respectively. The amount of the oil added to prepare the polyolefin solution was increased with increasing the molecular weight and content of UHMWPE given the solubility effect which accompanied the increase in viscosity. Other important factors in preparing a high concentration polyolefin solution containing an UHMWPE is the mixing method and the stirring conditions. These factors determine uniform drawability during the stretching treatment.

The mechanical strength of the separator as a function of draw ratio, is shown in Fig. 1, together with the dependence on the content and molecular weight of an UHMWPE contained in a polyolefin blending solution. The mechanical

strength of the separator increases sharply with mixing more than 10 wt.% UHMWPE with a molecular weight of 2 400 000 and 3 400 000 in the polyolefin composition, as is shown by curves (2)–(4). Adding UHMWPE ($M_w = 3\,400\,000$) produces a separator with a breaking strength of 650 kg cm^{-2} at a draw ratio of 4. The mechanical strength of the separator increases with increasing molecular weight and content of UHMWPE in the polyolefin composition solution. Adding 6 wt.% UHMWPE ($M_w = 3\,400\,000$) gives a separator with a breaking strength of 1000 kg cm^{-2} at a draw ratio of 5 (see curve (4)). Since the use of UHMWPE can cause an increase in viscosity and exert an adverse effect on the stretchability in a subsequent drawing step, the content of UHMWPE should be carefully controlled. In the present study, drawing can be made with a polyolefin composition solution which has up to 10 wt.% UHMWPE. Experiments, however, were performed at a concentration lower than 6 wt.% UHMWPE given the pore size and other properties. Different draw ratios in the range 2–4 were used for samples 1–3 considering the optimum drawability. The crystallinity in the drawn polyolefin was determined by DSC. The crystalline temperature was found to be $129.8\text{ }^\circ\text{C}$ (Fig. 2).

Puncture strength is another important property of the separator that is needed to prevent an internal short-circuit due to the formation and growth of dendrites. This shut-down (SD) function is essential for separators used in lithium batteries. Puncture strength is defined as the maximum load required on a given needle to puncture a given separator. The comparative puncture strength values of two, $25\text{ }\mu\text{m}$ thick, samples prepared by blending UHMPE of molecular weight 2 400 000 with HDPE, and UHMWPE of molecular weight 3 400 000 with HDPE in a ratio of 3:27, respectively, are given in Fig. 3. Puncture strength of the separator which

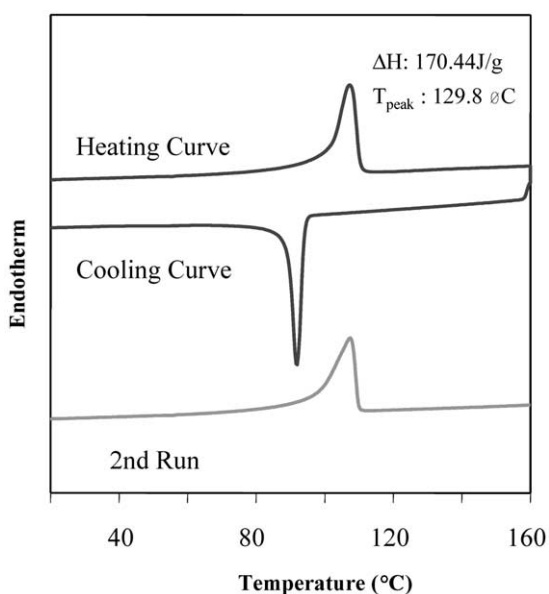


Fig. 2. DSC thermogram; sample 3.

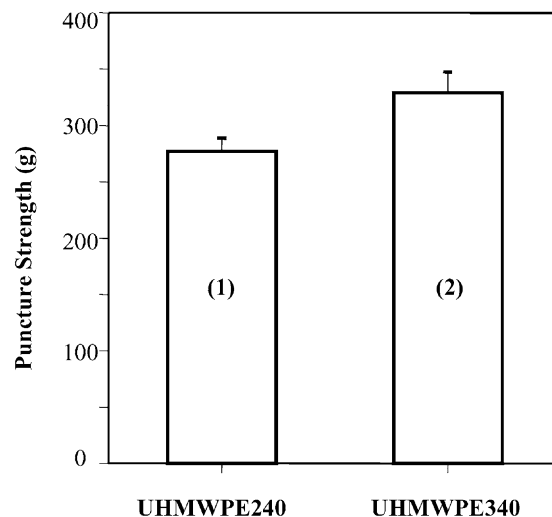


Fig. 3. Puncture strength according to polymer blending (HDPE: UHMWPE = 27:3); (1) sample 1 (UHMWPE, $M_w = 240\,000\,000$); and (2) sample 3 (UHMWPE, $M_w = 340\,000\,000$).

contains a higher molecular weight UHMWPE has a higher value than that which has a lower molecular weight UHMWPE. Similar trends have been observed from the mechanical strength data. The puncture strength of the separator with a higher molecular weight UHMWPE decreases with increasing draw ratio and consequently, decreasing thickness of membrane, as illustrated in Fig. 4. From these results, it is found that the puncture strength is directly related to the mechanical strength and is influenced by the size and distribution of the pores even though two samples exhibit the same mechanical strength. The puncture strength seems, however, to be more influenced by the mechanical strength than the structure of the pore given the even structure of the pores in the samples examined in this study.

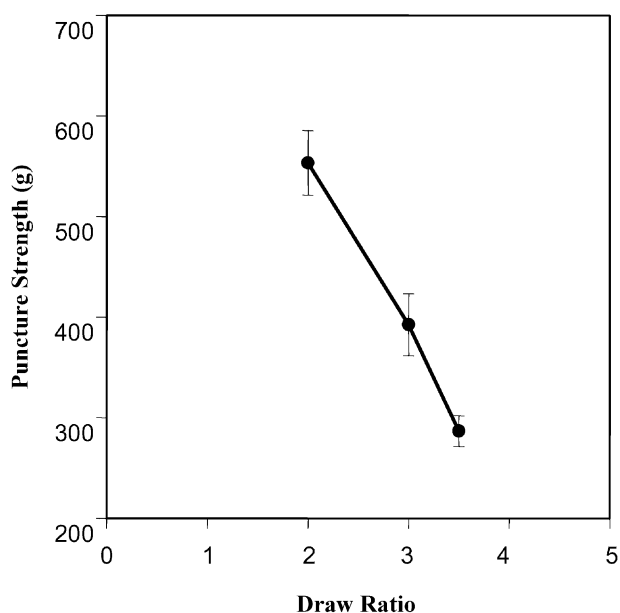


Fig. 4. Puncture strength according to draw ratios; sample 3.

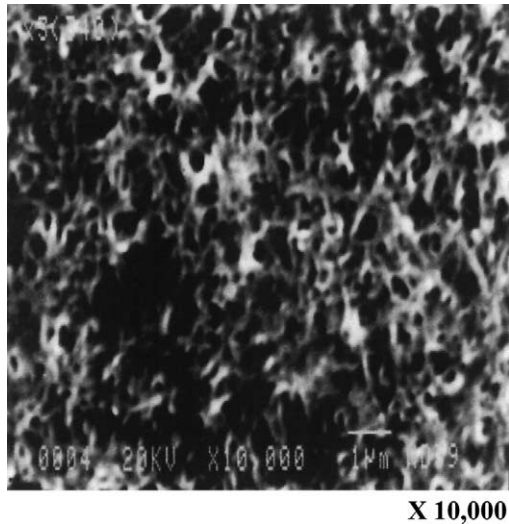


Fig. 5. Election micrograph of surface (10 000 \times); sample 3.

For a Li-ion separator, a pore structure which consists of small and uniform pores is preferred, since these pores act as a passage for Li-ions to and from the cathode and anode during the charge–discharge cycle. The combination of increased porosity (larger pore size) and dendrite formation limits the battery's ability to cycle and introduces significant safety problems. This is because dendrites that form can penetrate through the separator and cause a direct contact or short-circuit between the anode and cathode. The pore structure of the separator as studied by scanning electron imaging and porusimetry is shown in Figs. 5 and 6, respectively.

The pore structure shown in Fig. 5 is uniform throughout the bulk and the average pore size ranges from 0.1 to 0.12 μm . The mechanical strength and pore structure are influenced not only by the polymer composition solution but also by the stretching conditions such as drawing temperature, drawing speed, and draw ratio. The mechanical strength increases with increasing draw ratio. Quantitative

measurement of pore size distribution was made using an Auto-perm porometer. The pore-size distribution of the separator produced by the process of extraction after drawing is presented in Fig. 6, curve (1), while that produced by the process of drawing after extraction is given in Fig. 6, curve (2). The former process produces a separator with a pore size which ranges from 0.1 to 0.13 μm and the latter produces a separator with a pore size from 0.24 to 0.34 μm . This result is in good agreement with that reported by Mitsui Chemical and Asahi Chemical who adopted the process of drawing after extraction and Tonen who have claimed to make their separators by the process of extraction after drawing. The separators produced by the process of drawing after extraction are found to have much larger pore size and wider pore-size distribution than those produced by the process of extraction after drawing.

A SD function is another important characteristic of separators for lithium batteries. The function of increasing electric resistance in the case of a temperature rise due to an abnormal current to shut-off a battery reaction which thereby, prevents a further temperature rise for security is generally called a SD function. If it is too low, an increase in temperature initiates on a slight temperature rise, making the battery impractical. If it is too high, security is insufficient. The SD characteristics of the separator according to our experiment are shown in Fig. 7. It is seen that a sudden increase in resistance occurs around 130 $^{\circ}\text{C}$, which suggests that at this temperature the pores start to melt and the surface area for transporting the ions decreases considerably. The fuse layer melts and loses porosity at elevated temperature, which effectively stops current flow between electrodes. At 160 $^{\circ}\text{C}$, another change in the resistance value is observed. This temperature region may be regarded as an indication of a function of film form retention. In other words, the separator is melted by heat and it no longer retains its film shape, is broken, decreases its resistance, and loses its SD function. Therefore, from a safety consideration, it is necessary for a battery

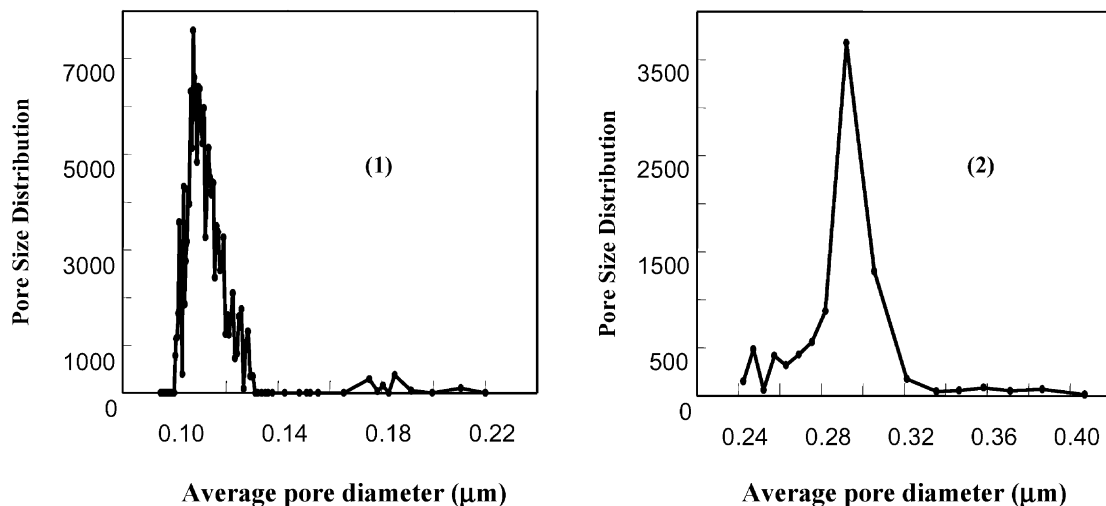


Fig. 6. Pore-size distribution of separator measured by porometer; sample 3: (1) solvent extraction after extension; and (2) extension after solvent extraction.

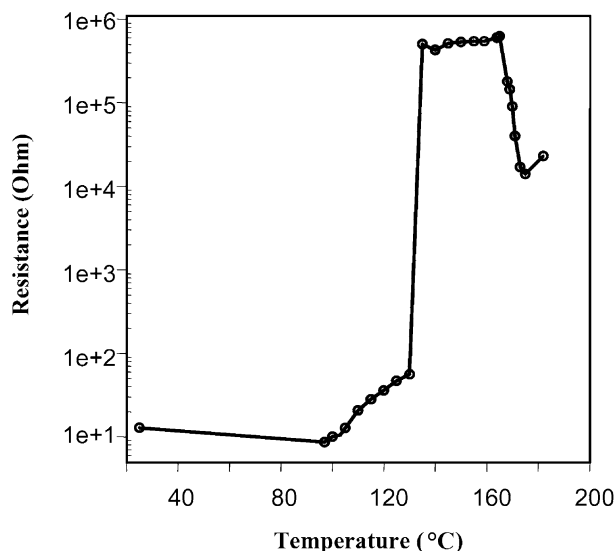


Fig. 7. SD curve; sample 3.

separator to have an SD initiation temperature which ranges from 130 to 160 °C, and a high heat resistance temperature with a broad heat resistance range. The temperature at SD initiation and loss of film form is influenced by the crystallinity and the pore structure. The SD temperature decreases with low crystallinity and dense pore-size distribution.

4. Conclusions

A wet process is used to make separators which contain a blend of HDPE and UHMWPE with a ratio of 9:1. The

mechanical strength and drawing characteristics are influenced by the content and the molecular weight of the UHMWPE contained in a polyolefin blending solution. In particular, a polymer solution which contains 6 wt.% UHMWPE produces a separator with a breaking strength of 1000 kg cm⁻² at a draw ratio of 5. The porous film produced by the process of extraction after drawing is found to have pore size which ranges from 0.1 to 0.13 μm with a satisfactory appearance free from unevenness. A separator comprised of this porous film performs a SD function; it shows a sudden increase in resistance around 130 °C and a fusion temperature around 160 °C.

References

- [1] Mao Xu, in: Proceedings of the Fifth Pacific Polymer Conference, 1997, p. 10.
- [2] R. Callahan, W.C. Yu, M. Geiger, C. Dwiggin, H. Fisher, D. Hoffman, K.M. Abraham, M.H. Jillson, T.H. Nguyen, in: Proceedings of the 11th International Seminar on Primary and Secondary Battery Technology and Applications, 1995.
- [3] Tonen, Jpn. Patent 8-12799.
- [4] S. Bierenbaum, B. Isaacson, L. Druin, G. Plovan, Ind. Eng. Chem. Prod. Dev. 13 (1974) 2–9.
- [5] Marketing report of Li-ion battery, Nomura Research, 1997, p. 3.
- [6] S.S. Kim, D.R. Lloyd, J. Membr. Sci. 64 (1991) 13–29.
- [7] Li-ion secondary battery materials and its applications, Jpn. Ind. News 91 (1996).
- [8] Hoechst Celanese, US Patent 3,558,764.
- [9] Nitto Denko, US Patent 5,385,777.
- [10] Tonen, Jpn. Patent 63-273651.
- [11] Asahi-Kasei, Jpn. Patent 8-64194.