NEW SYSTEMS FROM THE FORCED ASSEMBLY CO-EXTRUSION PROCESS

by

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New Systems from The Forced Assembly Co-Extrusion Process

XINTING WANG

Abstract

Development of continuous micro-/nano-fibrous composite tapes was achieved by a novel forced assembly co-extrusion process. The co-extrusion process was combined with 18 vertical and 5 horizontal multipliers, producing a unique structured tape which comprises a cross sectional matrix of 8192 x 32 individual polymer A and B domains. The tape could be post oriented to achieve enhanced mechanical properties due to their continuous feature in the extrusion direction. The domains could be mechanically separated by high pressure water jet if separating layer C is introduced before the horizontal multiplication. Different systems were developed for different applications in this work.

In Chapter One, polypropylene/high-density polyethylene (PP/HDPE) and polypropylene /polyamide 6 (PP/PA6) systems with polystyrene (PS) as the separating layer were studied for alkaline battery separator applications. PP/HDPE and PP/PA6 dual-component fibrous separators were fabricated by delamination of oriented PP/HDPE/PS and PP/PA6/PS tapes which were produced from force assembly co-extrusion. The separators had average pore size of 10 µm, high porosity and high surface area. The electrolyte absorption (KOH uptake) of PP/HDPE separators and PP/PA6 separators were almost 3 times higher than that of commercial separators. The battery performance of the PP/HDPE separators and the PP/PA6 separators were evaluated in a coin cell battery configuration. The charge-discharge efficiency of coin cells made from the PP/PA6 separator was found to be 6% higher than the commercial separators.

In Chapter Two, the orientation of PP/HDPE tape system was studied because both polymers could be oriented into strong fiber. The structure of the PP/HDPE tapes consists of cocontinuous PP and HDPE domains which are elongated in the extrusion, forming fiber-like structure with individual domain thickness of 200 nm to 500 nm in the extrusion direction. This unique structure creates extra-large contact area between the two components. AFM images suggest strong interactions between incompatible PP and HDPE. PP and HDPE crystallize at the same temperature, indication epitaxy between the two components. Orientation near the melting point of HDPE at 130°C is made possible because of the enhanced adhesion due to epitaxial crystallization and large interactive area between PP and HDPE. Modulus, tensile strength and orientation factor increase as draw ratio increase. Existence of shish-kebab like morphology in oriented tapes at different draw ratios is indicated by the two melting peaks. After one-step orientation at 130°C to draw ratio of 25, the moduli of oriented tapes increase to around 10 GPa and the tensile strength increased to about 540 MPa. These oriented tapes are stiffer and stronger than various commercial tapes and did not fibrillate during orientation.

In Chapter Three, poly (ethylene-co-methacrylic acid) sodium-neutralized ionomer (Surlyn 8940) fibers were produced from Surlyn/PS system. The PS matrix material were removed by toluene extraction to yield independent Surlyn fibers. The tensile properties of Surlyn fiber strands were studied under different strain rates. Surlyn fibers were oriented to 300% strain at different temperatures to study the effect of orientation on the tensile properties. The oriented Surlyn fibers were annealed after orientation to further enhance the mechanical properties. Further drawing of these oriented fiber mats to a draw ratio of 4 at 60°C followed by annealing at 60°C can afford moduli in excess of 350 MPa and tensile strengths in excess of 70 MPa.

Chapter 1

Alkaline Battery Separators with High Electrolyte Absorption from Forced Assembly Co-Extruded Composite Tapes

1.1. Introduction

Battery separators are membranes between positive and negative electrodes separating the negative and positive electrodes physically preventing electronic flow and permitting the ionic flow chemically. Typically, a battery is composed of cathode, anode, battery separator and ionic conductive electrolyte solution. Considering the components in the battery, the separator is a reservoir for the electrolyte and a physical barrier separating anode and cathode. Consequently, the separator insolates electronic flow and transports ionic flow at the same time. The separator influences the key parameters of the batteries¹ although the separator itself is an inert component in the battery not participating in the electrochemical reaction. The separator has direct influence on charge efficiency, discharge capacity and cycle life of the battery. Poorly performing separators weaken the battery performance and even lead to premature battery failure. Therefore, it is of vital importance to choose an appropriate separator and to improve the properties of the separator.

Recently, alkaline batteries have been under-emphasized even though the alkaline battery market is worth 7.25 billion U.S. dollars globally². In alkaline battery systems, nonwoven separators are commonly used. Nonwoven separators are nonwoven material made from polyolefin or polyamides. The production of nonwoven material contains three steps³: (1) web formation by drylaid, wet-laid, spun-bond or melt-blown; (2) web bonding by bonding agents, thermos-bonding, needling or hydro-entanglement; (3) post treatment to improve the wettability and thickness uniformity, change the thickness of the web, or introduce functionality by grafting acrylic acid or sulfonation.

Dry-laid process produce nonwovens separators from fibers with $10~20 \ \mu m$ diameter and 30~60 mm length by carding machines, consolidating fiber webs by fiber oil. The fiber oil gives the separator good initial wettability. However, the fiber oil could be decomposed in the chargingdischarging process of the battery, resulting in fading of the capacity of the battery³. Dry-laid process produces separators with coarse fibers which have good wettability and compressibility, but the separators suffer from low homogeneity. Wet-laid process is similar to paper production but using low viscosity short-cut fibers paste instead. The fibers used in wet-laid process have length less than 15 mm and diameter smaller than 10 µm. The separators from wet-laid process have excellent homogeneity but poor wettability because the fiber oil is washed out during the process. Spunbond and melt-blown are similar process that produce fibers from polymer melt extruded through the nozzles except that the fibers are pulled by hot air in melt-blown process. Spun-bond process produces fiber with around 11 µm fiber size while the melt-blown process produces fiber with less than 5 µm diameter. Post treatment is indispensable for both process when polyolefins are used as fiber materials. The homogeneity of separators from spun-bond process is not as good as wet-laid process. Separators from melt-blown process have improved homogeneity but low mechanical strength. More detail information about nonwoven processing are summarized in a book⁴. Currently the preferred technique for producing nonwoven separators is wet-laid process combined with thermal bonding.

The requirements of alkaline battery separator differ between different type of alkaline battery systems with different electrode materials. But some basic requirements of all alkaline battery systems are the same. Generally speaking, nonwoven separators having a thickness of 80~300 µm, a porosity around 70% and a maximum pore size over 10 µm meet the requirement of alkaline batteries³. Smaller pore size is favorable to avoid penetration by dendrites in some battery systems in order to improve the cycle life of the battery. Higher porosity results in higher the electrolyte uptake capability and lower ionic resistance of the separator, which improves charge-discharge capabilities of the battery. The wettability of the separator influences the battery production and battery cycle life. If the separator lost the wettability, the battery might fail prematurely and results in short cycle life. The electrolyte uptake is of vital import for the alkaline batteries, especially for nickel-metal-hydride system. In nickel-cadmium system and nickel-metal-hydride system, the electrolyte is consumed during the charge-discharge process and a separator with high electrolyte uptake could avoid the drain out of electrolyte.

The potential development of nonwoven separators is also promising. Nonwoven separators can be modified via surface chemical modification ^{5–7} to further improve the battery performance or laminated with a microporous membrane^{8,9} to achieve a more sophisticated function. Nonwoven separators have also been combined with nanoparticles^{10–12} or dip coated with polymer particles¹³ to be used as lithium type battery separators. The use of nonwoven separators as functionalized substrate has also been fulfilled by coating he nonwoven separators with ion-exchange polymers¹⁴.

Recently, a novel polymer continuous fiber fabrication technique was developed by utilizing co-extrusion and multiplication technique^{15–21}. Utilizing this method, PP/PA6 fibrous filters were produced with a thickness of 0.6 mm, a pore size of 12.5 to 128 µm and a porosity of

92.1%²². This unique technique was further explored and fibrous materials with a thickness of around 0.2 mm, mean flow pore size of 1 μ m and a porosity of 68% was attained. The thickness, pore size and porosity of the fibrous filter meet with the general requirement of alkaline batteries. The nonwoven separators are webs made from micro-fibers bonded together by either bonding agent or thermos-bonding. The fibrous filters are fiber mats made from micro to nano size fibers entangled with each other. Both nonwoven separators and fibrous filter have a fiber around empty space type of structure. The differences between the two are that (1) the fibers of the fibrous filters are rectangular rather than cylindrical, (2) the fibers are entangled with each other rather than welded by bonding agent or thermal treatment.

Inspired by the similarity between both nonwoven separators and fibrous filters, PP/HDPE and PP/PA6 nano-/micro-fibrous separators were produced for alkaline battery applications. The fabrication technique of PP/HDPE and PP/PA6 nano-/micro-fibrous separators involves no solvent and produces rectangular shape three-dimensional entangled fibers instead of flat fibers in traditional process. This structure and fiber morphology provide more surface area and smaller pore size than current technology, which could result in a better wettability. What's more, the fabrication technique is scaled-up in this work for the battery separator application. PP/HDPE and PP/PA6 nano-/micro-fibrous separators are tested in nickel-metal-hydride coin cell to verify the effect of wettability on the battery performance.

1.2. Experimental Section

1.2.1. Materials

The materials used were Polypropylene (PP), (Exxon Mobil 2252 E4); high-density polyethylene (HDPE), (Dow Elite 5960 G). The Polyamide 6 (PA6), (BASF Ultramid B 36 01) was dried at 80°C for 24 h in a vacuum oven before processing. Polystyrene (PS), (Dow 685 D) was also used as the separating material in the composite tapes. The PP used in this study is a homopolymer recommended for woven fabric applications with a density of 0.90 g/cm³. The densities of HDPE, PA6 and PS are 0.96 g/cm³, 1.13 g/cm³ and 1.04 g/cm³ respectively.

1.2.2. Preparation of Polymeric Fibrous Battery Separators

The fabrication of alkaline battery separators is divided into four major steps: (1) processing of the PP/HDPE/PS and the PP/PA6/PS fibrous tapes; (2) post processing orientation of the fibrous tapes; (3) high pressure water delamination of 90° cross-plied oriented tapes; and (4) corona discharge treatment of the fibrous membranes from step (3).

1.2.2.1 Co-Extrusion of Composite Tapes

As shown in Figure 1.1, polymer A and polymer B are melt fed into separate single screw extruders and co-extruded through an A/B feedblock. The materials from both extruders are conveyed to the feed block which aligns the two polymer melts in the multiplier. The polymer melt from extruder A co-flows upon the polymer melt from extruder B and the combined melt having a two-component horizontal-layered structure is aligned vertically by the first multiplier in Step I. The vertical multiplication step is repeated in Step II. In this vertical multiplication step, the polymer melt is divided horizontally forming two independent polymer melt flows. The two flows are spread and recombined. As a result, the vertical polymer layer number doubles after this vertical multiplication step. The number of vertical multiplications (n) can be varied in Step I and II to obtain 2^n vertical layers. After vertical multiplication, the surface layer of PS is added to the top and bottom of the melt surface in Step III. Next, the flow with 2^n vertical layers are sandwiched between PS surface layers and multiplied horizontally m times in Step IV using the same multiplier mechanism used in Step I and II. In Step IV, the vertical layer is decreased by one half of the initial layer number after each horizontal multiplier due to the division and recombination in the vertical direction. This process produces a composite polymer melt with 2^m horizontal layers of A/B polymers (A/B 2^{n-m} alternating A/B domains) and $2^m + 1$ separating horizontal layers. After multiplication, the continuous 0.5" x 0.5" melt flow of A/B/PS is extruded through a 3" film die and cooled on a chill roll having constant temperature. The thickness of the composite tape can be further adjusted by changing the speed of the chill roll.

In this study, PP/HDPE/PS and PP/PA6/PS composite tapes were produced using the above method under different processing conditions. 18 verticals and 5 horizontal multipliers were used to produce 8192x32 PP/HDPE fiber domains. PP/HDPE/PS composite tapes with volume fractions of 45/45/10 were produced at 250°C with a 3" die and collected on a 90°C chill roll producing tapes with a thickness of 300 µm. The PP/PA6/PS composite tapes with volume fractions of 45/45/10 were produced at 255°C with a 3" exit die and collected on an 80°C chill roll producing tapes with a thickness of 130 µm.

1.2.2.2 Post Production Orientation of Composite Tapes

After the co-extrusion process, the composite tapes were oriented to enhance the mechanical properties of fiber domains using mechanical testing machine (MTS Alliance RT/30)

with temperature controlled environmental chamber. The orientation temperature was selected above the glass transition temperature of PS at 102°C and just below the melting temperature of one of the fiber domains. Based on previous study^{22,23}, 130°C was determined as the best orientation temperature for both the PP/HDPE/PS and the PP/PA6/PS fibrous tapes. The orientation temperature of PP/HDPE/PS and PP/PA6/PS tapes were illustrated in the differential scanning calorimetry thermograph in Figure 1.2. The PP/HDPE/PS tapes were oriented at 130°C and a strain rate of 1000%/min to a draw ratio of 15. The PP/PA6/PS tapes were oriented at 130°C, 1000%/min strain rate and were drawn to a draw ratio of 4.

1.2.2.3 Delamination of Oriented Composite

After the high temperature orientation, the oriented tapes were combined into a two-ply structure with the tapes aligned at 90°. The two-ply oriented tapes were combined to 10" by 10" square shape and placed between two pieces of metal mesh as shown in Figure 1.3(a). Mechanical separation of the fibers was achieved by using high pressure water. The water was pumped into the system purchased from Atomizing Systems, Inc. to build up high pressure. Then the high pressure water flowed through the nozzles arranged as shown in Figure 1.3(b). The nozzles have a diameter of 0.010". The metal meshes containing the sample tapes were placed 3" below the nozzles on the stage as shown in Figure 1.3(b). The two-ply oriented tapes were washed in the X-direction at a linear speed of approximately 0.5" per second. When the X-direction wash was finished, the stage then moves the sample 0.01" in Y-direction and then repeating the wash process in the X-direction. The stage is controlled by a stepper motor control having a programmable logic

controller (PLC). The cross-ply sample was inverted after initial washing and then subjected to similar wash conditions to obtain the PP/HDPE and PP/PA6 separators for corona treatment.

1.2.2.4. Corona Treatment

In order to improve the wettability of the untreated PP/HDPE and PP/PA6 separators, the surface was modified by corona treatment. A corona discharge generator with an output power of approximately 25,000V was positioned above the surface of the separators. The field effect electrode was selected because it is recommended for treating thick or irregularly shaped surfaces. The distance between the tip of electrode and the separator was fixed at ¹/₄" as suggested by the manufacturer. The separators having 2" by 5" dimensions were treated for different lengths of time in order to investigate the effect of corona treatment time on separator wettability.

1.2.3. Characterization Methods

The crystal orientations of PP/HDPE/PS and PP/PA6/PS as-extruded and the oriented tapes were characterized by a 2D Wide Angle X-ray Diffraction (WAXD) unit from Rigaku with Cu-Kα X-ray source. The sample to detector distance is 40 mm. In all characterizations, the X-ray beam is aligned vertically to the extrusion direction of in the thickness direction fibrous tape. The data were collected on the image plate with 10 seconds beam time exposure.

The surface morphology and fiber size were determined using scanning electron microscopy (SEM, JEOL-JSM-6510LV). Samples were sputter coated with a 5 nm thick gold layer. SEM images were taken at different positions on the separator surface and 100 different fibers were measured to determine the average fiber size.

The pore sizes of all materials were measured using through-pore characterization following ASTM F316 using a Porometer 3G Macro instrument from Quantachrome (Boynton Beach, FL). The materials were treated with "Porofil[®]" liquid before each test and the test parameters were based on a pore size range of $1 \sim 300 \,\mu\text{m}$ and the thickness of the sample. Each test consisted of a wet run using a wetted sample and a dry run using a dry sample. The maximum pore size is defined as the first bubble point from the wet analysis. The minimum pore size is determined by the cross membrane pressure of first point where wet analysis curve and dry analysis curve coincide. The mean flow pore size is derived from the cross-membrane pressure of the middle point of the dry analysis curve which does not overlap with the wet analysis curve. The thickness of each sample was determined using the average of ten measurements at different locations on the separator sample using a micrometer.

The porosity was determined by the density method usually used in battery separator characterization as defined in eq. 1, where ρ_{hulk} is the density of separator, $\rho_{nolymer}$ is the density

$$Porosity = \left(1 - \frac{\rho_{bulk}}{\rho_{polymer}}\right) * \ 100\% = \left(1 - \frac{m_{separator}}{(\rho_{PP} + \rho_{HDPE})/2}\right) * \ 100\% \ (1)$$

of the composite tapes. ρ_{filter} is determined by the weight over volume of the separator; $\rho_{polymer}$ I is the average density of PP and HDPE. In the case of PP/PA6 separator, $\rho_{polymer}$ is the average density of PP and PA6.

The wettability was characterized by determining the water contact angle of the materials using a video contact angle measuring system. Water droplets with 2μ L volume were placed on the surface of samples and images for contact angle determination were captured after 10 seconds. Electrolyte uptake of the separator is defined in eq. 2, where W_1 is the weight of separator after immersion in 30%wt potassium hydroxide (KOH) electrolyte solution for 2 minutes and W_0 is the initial weight of separator. Before weighing, the separator was dabbed on the beaker wall to remove the extra electrolyte.

Absorption =
$$100\% * (W_1 - W_0)/W_0$$
 (2)

The Brunauer-Emmett-Teller (BET) method was used to measure the specific surface area. The BET method is widely used to measure specific surface area based on the single layer physical absorption of an inert gas. The BET surface area of the separators was measured by a Micromeritics Tristar II unit (Norcross, GA) using the krypton gas analysis method. All samples were weighed and degassed under a nitrogen environment at 70°C for 24 hours before the test.

1.2.4. Mechanical Test

Tensile properties of the separators were measured by using Instron 5965 unit following ASTM D828. The tensile modulus was defined as slope of the initial linear region within 2% strain and was automatically calculated by the machine. All tests were conducted at room temperature with a gauge length of 50.8 mm and a width of 25.4 mm at 25.4 mm/min strain rate.

1.2.5. Battery Test

Coin cell cases with positive and negative cap, spring and spacer were purchased from Gelon Lib Co, Limited. The positive electrode was nickel oxide hydroxide sintered on a stainlesssteel grid. The electrodes were prepared by standard methods described in the literature²⁴. The negative electrode was LaNi₅ alloy on a nickel foam produced by a wet spreading method. The diameter of both positive and negative electrodes were 1/2". The diameter of the separator was cut into ³/₄". The separator was then wet by 30%wt potassium hydroxide solution (from Fisher Scientific) and placed between the two electrodes. The separator was pre-soaked in the electrolyte solution for 2 minutes in 6M electrolyte before placing into the coin cell, which is consistent with the electrolyte uptake measurement. The coin cells were sealed by a coin cell sealing machine from Gelon Lib Co, limited. A commercial alkaline battery separator was used as a control sample for the polymeric separator comparison. The assembled coin cells were tested on a battery testing system (Gelon Lib Co, limited) at a 0.1 C charge-discharge rate. Following standard procedures, the coin cells were charged for 10 hours or charged until the voltage of the coin cell reached 1.6 V (whichever occurs first), followed by a 20 minutes' rest period and then discharged for a period of 10 hours or until the voltage of the coin cell reached 1.0 V (whichever occurs first).

1.3. Results and Discussion

1.3.1. Fabrication of Alkaline Battery Separators

1.3.1.1 Effect of Post Processing Orientation

The high temperature orientation step was designed to improve the mechanical properties of the fiber and decrease the fiber size at the same time. Therefore, the drawing temperature was chosen to when the composite tape achieved the highest draw ratio without breakage. Different temperatures were scouted between 102°C and 133°C. For PP/HDPE system, the highest draw ratio reached at 110 °C, 120°C and 130°C were 16, 19 and 20 respectively. For PP/PA6/PS system, the orientation condition was based on our previous work^{22,23}. The effect of orientation upon the tapes at high temperature were evaluated by comparing the WAXD pattern of the tape before and after orientation.

In the WAXD pattern of as-extruded PP/HDPE/PS tapes in Figure 1.4(a), there is a PS amorphous halo and isotropic oriented rings in the pattern which can be assigned to the PP (110), (130), and (111/041) reflection planes and the HDPE (200) reflection plane, respectively. This indicates that the polymer crystals are randomly orientated in the PP/HDPE/PS tapes. After orientation to a draw ratio of 15 in the fiber direction, sharp reflections are observed at $2\theta = 14.1^{\circ}$, 17.0° , 18.5° , 21.4° and 24.0° in Figure 1.4(b). Reflections at $2\theta = 14.1^{\circ}$, 17.0° and 18.5° represent the PP α (110), (040) and (130) respectively. The reflections at $2\theta = 21.4$ and 24.0 are represent the HDPE (110) and (200). This indicates that the crystals of PP and HDPE are highly oriented.

Regarding the as-extruded PP/PA6/PS tapes, reflections of PP (110), (040), (130) and (111/041) were observed in the WAXD pattern as isotropic oriented rings. Clear crystal reflections from PA6 were not detected in as-extruded PP/PA6/PS tapes. Similar to PP/HDPE/PS as-extruded fibrous tapes, crystal orientation of PP and PA6 were randomly oriented in the as-extruded tape structure. When oriented to a draw ratio of 4 at 130°C, sharp reflections are observed on the equator in the WAXD pattern as shown in Figure 1.4(d), which indicates that PP and PA6 crystallites are highly oriented. The reflections at $2\theta = 14.2$, 17.0 and 18.6 represent the PP (110), (040) and (130); reflections at $2\theta = 20.6$ and 23.1 represent the PA6 α (200) and α (002/202).

1.3.1.2 Delamination of Cross-Plied Oriented Tapes

Due to the difference in mechanical properties between fiber domain and matrix PS, the brittle glassy PS matrix fractured into small pieces upon impact by the high pressure water and were washed out of the tape. The uniqueness of this mechanical separation method is that no solvent is involved in the fiber fabrication process. This process can also be scaled up easily by incorporating more water nozzles and increasing the size of the moving XY stage. This process is also a well-established process in the industry and defined as hydro-entanglement. In this work, the untreated PP/HDPE and PP/PA6 separator samples were prepared with a dimension of 10" by 10".

The optimum delamination conditions were chosen as 1000 psi with XY moving stage speed of 150 rpm in both directions. After orientation and delamination, separators were fabricated with the morphology shown in Figure 1.5 (a) and (c). Both the untreated PP/HDPE separators and PP/PA6 separators have ribbon-like microfibers with similar fiber dimensions. The cross-section of those ribbon-like fibers are rectangular shaped, which introduces a larger surface area than traditional cylindrical non-woven fibers. Based on statistics of 100 fibers from different SEM images, the untreated PP/HDPE separators have an average fiber width of 3.9 µm and the untreated PP/PA6 separators have an average fiber width of 4.8 µm.

The pore size of the untreated PP/HDPE separator ranged from 8 μ m to 30 μ m, with a mean flow pore size of 10 μ m. The mean flow pore size of PP/PA6 fibrous membrane was also 10 μ m but in a narrower range between 6 μ m and 23 μ m. The maximum pore size of both separator types are all over 10 μ m which are suitable for the alkaline batteries³ as described in the introduction part. The contact angle, porosity, and BET surface area were similar for both types of separators as listed in Table 1.1. Both PP/HDPE and PP/PA6 separators were hydrophobic and exhibited a high porosity of around 85%. The BET surface area of the untreated PP/HDPE and PP/PA6 separator membranes were 2.42 m²/g and 2.62 m²/g, respectively.

1.3.1.3 Corona Treatment

Since commercial alkaline battery separators are treated to be hydrophilic, the hydrophobic separators produced in this work were treated using corona discharge. Hydrophilicity of the separator influences the wettability of electrolyte and therefore affects battery performance. The absorption capacity of the electrolyte influences the long term battery properties such as cycle life and self-discharge. The wettability of the separator is characterized by the contact angle and the absorption capacity is characterized by the KOH uptake. The effect of the corona treatment time on wettability was studied by correlating the treatment duration with the contact angle and KOH uptake. The relationship between treatment time and wettability is plotted in Figure 1.6. As the corona treatment duration increases from 0 to 20 second, the water contact angle of the PP/HDPE fibrous separator decreases from 126° to 103°. When the treatment duration is 25 s, the water contact angle goes to 0°. The KOH uptake increases rapidly with increasing treatment time and reaches a plateau when the separators have been treated for 60 s.

The contact angle decreases from 132° to 0° after 5s of corona treatment for PP/PA6 fibrous separator. The transition of the wettability for the PP/PA6 separator requires less treatment time than the PP/HDPE fibrous separators because the PA6 is more hydrophilic than HDPE. The KOH uptake also plateaus around 1585% after 25 s corona treatment. After corona treatment, the PP/HDPE separators have a wettability of 1355%. The PP/PA6 separators exhibit a wettability of 1585%.

1.3.2. Mechanical Properties

Mechanical properties are important in the battery manufacturing process because the speed of battery assembly is limited by the mechanical strength of the separators. Separators

having higher tensile strength could be processed faster so that battery assembly can be faster. As shown in Figure 1.7, the commercial separators had anisotropic mechanical properties along the machine direction and transverse to the direction. The PP/HDPE and PP/PA6 separators demonstrated isotropic mechanical properties in both directions reflecting the 90° cross-plied stacking of two oriented tapes. In the machine direction, the tensile modulus of the commercial separator was 189 MPa, while in the cross direction, the tensile modulus was 77 MPa which is only 40% of the machine direction value. The tensile strength also decreased from 8 MPa in the machine direction to 3 MPa in cross direction. The tensile modulus of the PP/HDPE separator was 248 MPa which is almost 1.5 times that of the tensile modulus of the commercial separator in the machine direction. The tensile strength of PP/HDPE separator was 14 MPa, which is almost 5 times higher than the tensile strength of commercial separators in the cross direction. Although the PP/PA6 separator had a lower tensile modulus, its tensile strength is similar to the tensile stress of commercial separator in the machine direction and higher than the tensile stress of commercial separator in the cross direction. The stress-strain curves of both the PP/HDPE and the PP/PA6 separators showed a gradual fracture after the maximum load. The commercial separators fractured abruptly after 20% strain. This indicates that the PP/HDPE separators could provide more load before fracture compared to the commercial separator. The detail statistics of mechanical properties and the error bar based on 5 samples were summarized in Table 1.2.

1.3.3. Comparison with Commercial Separators in Terms of Structure, Morphology And Properties

Commercial battery separators are PP and HDPE dual-component nonwoven fiber mat produced from conventional fiber production techniques. The fabrication method of the commercial separator was not disclosed but could be produced by dry-laid, wet-laid or melt-blown techniques. Dry-laid fiber separators have good wettability but suffer from low homogeneity. Wetlaid fiber separators have excellent homogeneity but bad wettability. Melt-blown fiber separators have small pore sizes and good homogeneity but generally have weak mechanical properties. In contrast, PP/HDPE and PP/PA6 separators have very homogeneous structure and demonstrate excellent wettability and enhanced mechanical properties.

As can be observed in Figure 1.5, the PP/HDPE and PP/PA6 separators have different morphology than the commercial separators. Commercial separators exhibit flat fibers due to the thermal bonding process. The PP/HDPE and the PP/PA6 separator fibers are more entangled than the commercial separator. This entangled structure provides better mechanical strength to the separator than the untangled structure because it provides more ductile and stronger fiber-fiber contact points than thermal bonding. Compared to the 12.1 µm wide fibers of the commercial separators, the PP/HDPE and the PP/PA6 fibrous separators have a smaller average fiber size.

In order to validate the performance of the PP/HDPE and the PP/PA6 separators in an alkaline battery, a comparison was conducted with commercial separators. This structure and property comparison is summarized in Table 1.3. Note that the properties of PP/HDPE and PP/PA6 separators in Table 1.3 were the properties after corona treatment, which is different from the properties of untreated PP/HDPE PP/PA6 separators in Table 1.2. The properties of PP/HDPE and PP/PA6 separators are almost the same as properties in Table 1.2 except the contact angle. This indicates that the corona treatment only changes the hydrophilicity of the PP/HDPE and PP/PA6

separators and do not have effect on the other properties. After corona treatment, PP/HDPE and PP/PA6 separators are as hydrophilic as the commercial separator. The PP/HDPE and PP/PA6 separators are thicker than the commercial separator but are still in the same several-hundredmicron thickness range as the commercial separators. Compared with the commercial separator, the PP/HDPE and the PP/PA6 separators have smaller mean flow pore size and larger BET surface area. The smaller mean flow pore size can prohibit penetration by zinc dendrites³ in alkaline-manganese, nickel-zinc and zinc-air battery systems. The higher BET surface area and porosity give the PP/HDPE and the PP/PA6 separators a better capability to absorb more electrolyte. The electrolyte uptake of PP/HDPE and PP/PA6 separators were almost 3 times higher than that of commercial separators. The batteries made with separators demonstrating high electrolyte uptake have the potential to possess a longer cycle life according to the literature^{1,3}.

1.3.4. Battery Performance of Coin Cells Made from PP/HDPE, PP/PA6, And Commercial Separators

In order to evaluate the feasibility of alkaline battery separators, the battery performance of coin cells made from different separators were investigated. As shown in Figure 1.8, coin cells made from PP/HDPE and PP/PA6 separators demonstrate similar charge-discharge profiles as that of commercial separators. This indicates that PP/HDPE and PP/PA6 separators are suitable for consideration in alkaline batteries. When comparing the 10th discharge curves in Figure 1.9, it was found that co-extruded PP/HDPE and PP/PA6 separators exhibited longer stage voltage profiles and a higher discharge capacity. This enhanced performance of the PP/HDPE and the PP/PA6 separators is due to better electrolyte wettability, smaller pores and larger porosity than that of the

commercial separator. Better wettability and larger porosity imply that more channels could be offered to facilitate ionic transfer in the electrolyte. The smaller pores and more uniform pore size distribution facilitate a more even current distribution. All of these factors lead to the increase in the discharge capacity of the coin cells made from PP/HDPE and PP/PA6 separators.

The efficiency of the coin cells made using PP/HDPE, PP/PA6 and commercial separators after 100 cycles are 90%, 93% and 87% respectively (Figure 1.10). The PP/PA6 separator produced from the continuous co-extrusion technique improved the efficiency of the alkaline coin cells by 6% compared to the coin cells made from the commercial separator. This indicates that coin cells made from PP/HDPE and PP/PA6 separators have a better battery cycle durability due to the improvement in wettability. In addition, the coin cells made with the PP/HDPE and PP/PA6 separators have the potential to exhibit a longer cycle life because of the high wettability. However, the life time of the coin cells were not tested due to time duration of the tests.

1.4. Conclusions

PP/HDPE and PP/PA6 separators were successfully produced using a novel co-extrusion and multiplication technique following by a unique mechanical fiber separation method. This process could be scaled up to production because it is a continuous process and the technology involved is industrially available. Compared to the wet-laid process which is the standard separator processing technology for alkaline-manganese and nickel-metal-hydride batteries, this process involves no solvent. This battery separator fabrication technique also allows a wide choice of materials to fit into different alkaline battery systems due to the versatile co-extrusion processing. Compared to commercial alkaline battery separators, the PP/HDPE and PP/PA6 separators had higher surface area, smaller pore size and narrower pore size distribution. Such outstanding structure of PP/HDPE and PP/PA6 separators enables the electrolyte absorption beyond that of current existing commercial separators.

The coin cells made from the PP/HDPE and PP/PA6 separators perform similar to coin cells made from the commercial separator. This demonstrates that the PP/HDPE and PP/PA6 separators meet the fundamental requirements of commercial alkaline batteries. The efficiency of coin cell batteries made from the PP/HDPE and PP/PA6 separators demonstrated an efficiency 3% and 6% higher than the commercial separators respectively, illustrating a promising battery performance improvement caused by the PP/HDPE or PP/PA6 separator.

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Material	Max. pore size (µm)	Min. pore size (µm)	Mean flow pore size (µm)	Porosity (%)	Contact angle(°) (6M KOH)	BET surface area (m ² /g)*
PP/HDPE	30	8	10	85	126	2.42 ± 0.11
PP/PA6	23	6	10	84	124	2.62 ± 0.13

Table 1.1. Properties of PP/HDPE and PP/PA6 separator membrane

*The value of BET surface area is the mean value. The value after "±" stands for the standard deviation of the mean value.

	Young's Modulus[MPa]	Tensile stress at Maximum Load [MPa]
Commercial separator in machine direction	189±12	8±0.5
Commercial separator in cross direction	77 ± 6	3 ± 0.2
PP/HDPE separator	248±29	14 ± 0.5
PP/PA6 separator	61±6	8.6 ± 0.9

 Table 1.2. Mechanical properties of PP/HDPE separator, PP/PA6 separator, commercial separator in both machine and cross direction.

*The values are the mean value based on 5 measurements. The numbers after " \pm " stand for the standard deviation of the mean value.
Sample Name	Material	Contact Angle (6M KOH)	KOH Uptake (%)	Thickness (µm)	BET Surface Area (m ² /g)	Mean Flow Pore Size (µm)	Porosity (%)
Commercial separator	PP/HDPE	0°	576±69	279±9	$\begin{array}{c} 0.24 \pm \\ 0.01 \end{array}$	98 ± 7	79
Corona treated PP/HDPE separator	PP/HDPE	0°	1355±57	351±54	2.42 ± 0.11	10 ± 1	85
Corona treated PP/PA6 separator	PP/PA6	0°	1453 ± 63	408±42	$\begin{array}{c} 2.68 \pm \\ 0.16 \end{array}$	10 ± 2	84

 Table 1.3. Comparison of structure and properties of battery separators

*The values are the mean value based on 10 measurements. The numbers after "±" stand for the standard deviation of the mean value.



Figure 1.1. Schematic illustration of (a) co-extrusion and multiplication processing line for fibrous tape fabrication; (b) cross-sectional structure of the polymer flow in five stages corresponding to (a).



Figure 1.2. DSC thermograph of (a) PP/HDPE/PS as-extruded composite tape and (b) PP/PA6/PS asextruded composite tape.



Figure 1.3. Fabrication of separator from oriented composite tapes (a) arrangement of cross-plied oriented composite tapes under water jet; (b) mechanical separation of fiber domains using automatic high-pressure water jet.







(d)



(e)

Figure 1.4. Wide angle X-ray diffraction pattern of (a) PP/HDPE/PS as-extruded; (b) PP/HDPE/PS tape with draw ratio of 15; (c) PP/PA6/PS as-extruded tape (d) PP/PA6/PS tape with draw ratio of 4; (e) commercial separator.



Figure 1.5. Surface morphology of PP/HDPE separator from tapes with draw ratio of 15 (a) before corona treatment, (b) after corona treatment; PP/PA6 separator from tapes with draw ratio of 4 (c) before corona treatment, (d) after corona treatment; (e) commercial separator; (f) fiber size comparison. Scale bar = 50 μm.



Figure 1.6. The effect of treatment time on KOH uptake and contact angle on (a) PP/HDPE separator, (b) PP/PA6 separator.



Figure 1.7. Stress-strain curve of PP/HDPE separator, PP/PA6 separator, commercial separator in both machine and cross direction.



Figure 1.8. First 10 charge-discharge profile of coin cells using different separators in 1 C constant charge-discharge cycles (a) PP/HDPE fibrous separator, (b) PP/ PA6 fibrous separator, (c) commercial separator.



Figure 1.9. 10th Discharge Curves of the coin cells using PP/HDPE, PP/PA6, Commercial separators in constant charge-discharge cycles.



Figure 1.10. Comparison of efficiency of coin cells after 100 constant current charge-discharge cycles. The average values are based on 3 measurements; the error bars stand for standard deviation of the average.

Chapter 2

Oriented Tapes of Incompatible Polymers Using a Novel Multiplication

Co-Extrusion Process

2.1. Introduction

There are numerous publications and reviews on incompatible polymer blends with and without coupling agents emphasizing the vast area of structure-properties processing relationships using carefully designed macromolecular architectures. However, there are still relatively few fundamental studies on orientation of these systems leading to stiff and strong tapes. A pioneering paper by Gallagher et.al [1] suggested that blends of polyethylene (PE) and polypropylene (PP) when highly oriented yielded very stiff tapes even without the use of compatibilizers. More recently, Schmidt et.al. [2] still using conventional blend processing methodology, studied room temperature oriented blends of PE and PP which were subsequently annealed at temperatures slightly above the melting point of PE. As a result of annealing the PE chains were re-oriented perpendicular to the draw direction suggesting epitaxial growth of the PE on the PP [3,4,5]. Vice versa, evidence that PE can nucleate PP was provided by Bartczak et.al. [6] by studying primary nucleation of spherulites. It was observed that the primary nucleation mechanism was strongly dependent on the crystallization temperature. These observations suggest that either PE or PP can serve as epitaxial templates, that is, PE can crystallize on PP or PP can crystalize on PE.

These studies suggest that the epitaxial interface between PE and PP can promote the adhesion that is needed to create PP/HDPE tapes materials with superior properties and that

efficient melt mixing is required to produce large amounts of contact area between the two components. This idea was exploited by Polaskova et.al. [7] who created a unique extrusion die combined with counter-rotating twin-screw extruders. A micro fibrillar morphology was observed in the blend without further post orientation procedure. It was proposed that upon post extrusion orientation of these microfibrillar blends, tapes with enhanced mechanical properties could be produced.

The goal of this paper was to manufacture superior tapes from immiscible PE/PP by using the previously reported continuous nanofibers co-extrusion technique [8-12]. This technique is designed to systematically produce composite tapes with large amounts of surface area between two immiscible polymers. The large surface area promotes the contact between the two incompatible polymers thereby promoting the required adhesion. PE and PP were chosen for this study since both polymers can be oriented into strong fibers, and as previously noted, are known to epitaxial crystallize under various processing conditions.

2.2. Experimental Section

2.2.1. Materials

Polypropylene (PP), (Exxon Mobil 2252E4) and high-density polyethylene (HDPE), (Dow Elite 5960G) were used in this study. The PP is a homopolymer and has a density of 0.900 g/cm³. The HDPE was produced from metallocene catalysts and has a density of 0.962 g/cm³.

2.2.2. Co-extrusion of Tapes

The PP/HDPE tapes with 50/50 volume fraction were produced from a co-extrusion and multiplication system as shown in Figure 2.1 (a). The cross-sectional structure of the polymer melt in multiplication steps were illustrated in Figure 2.1 (b) and described as follow.

Equal amounts of PP and HDPE were extruded at 250°C from two single screw extruders simultaneously and fed into a feedblock producing a two horizontal layer configuration. In Step I, the PP/HDPE two-horizontal-layered melt was turned into the vertical direction after passing through the first vertical multiplier. The melt processed through 17 more vertical multipliers to achieve a structure with 2¹⁸ vertical layers as shown in Step II. After getting stabilized in a feedblock with a straight channel that has same cross-section shape as the multiplier, the melt went through 5 horizontal layer multipliers as shown in Step III. The melt in the horizontal multiplier, was cut in the center vertically into two independent melt flows upon entering the channel. The two flows were then twisted in the channel and finally stacked one on top of the other. Assuming that the melt was cut perfectly in the center at the entrance and the two melts did not recombine completely at the exit, after going through one horizontal multiplier, the vertical layer number decreased by half and the horizontal layer number increased by two. The aim for the 5 horizontal multipliers was to get a smaller domain size in the thickness direction. After going through 5 horizontal multipliers, a structure with 8192 x 32 number of domains was produced as shown in Figure 2.1(c). There are 8192 number of PP or HDPE domains in one horizontal layer and 32 horizontal layers in the thickness direction. In Step IV, the melt was spread by a 3" film die. The tape was then collected on a chill roll with a temperature of 90°C. The thickness was controlled by the speed of the chill roll and was fixed to 200 µm. Based on a 60 mm tape width, the theoretical domain size is 7.3 µm in width and 6.2 µm in thickness for both the PP and HDPE. The processing temperatures for the extruders, all the multipliers and the exit die were 250 °C.

PP control tapes and HDPE control tapes were produced using the same process and conditions as the PP/HDPE (50/50) tapes. Both A and B extruder were fed with same material while producing PP or HDPE control tapes. The tape dimensions for PP and HDPE control tapes were also kept the same as PP/HDPE (50/50) tapes.

2.2.3. High Temperature Orientation of Tapes

PP/HDPE (50/50) tapes, PP control tapes and HDPE control tapes were cut into 3cm x 8.2cm rectangular shapes before drawing. Those tapes were placed in an environmental controled chamber and drawn on a mechanical testing machine (MTS Alliance RT/30) with a gauge length of 12 mm and at a strain rate of 1000%/min. 80 grit emery cloth was attached to the jaw faces of MTS grips to avoid slipping during drawing. The temperature of the chamber was set to either 130°C or 110°C. The tape was heated for 10 minutes before drawing to equilibrate the temperature throughout the tape.

2.2.4. Tensile Measurements

The oriented PP/HDPE tapes and PP control tapes were embedded in the Emery cloth by using Super glue 15187 before the tensile measurements. The oriented HDPE tapes were embedded in the Emery cloth by using J-B Weld 50101 MinuteWeld Instant-Setting Epoxy before the tensile measurements. The aim for this sample preparation step was to avoid slipping inside the grips during the measurement. The mechanical properties of the oriented tapes were tested at room temperature at a draw rate of 100%/min by using Instron 5965 series universal testing systems in accordance with ASTM D882.

2.2.5. Structural Characterization

Differential scanning calorimetry (DSC) measurements were carried out using sealed aluminum pans on a TA Instrument Q2000 DSC unit. The DSC samples were heated from 25 °C to 200 °C and then cooled down to 25 °C with a ramp rate of 10 °C/min. A two-minute isothermal procedure was conducted before heating or cooling.

The crystal orientations of PP and/or HDPE domains were characterized by using a Rigaku 2D Wide Angle X-ray Diffraction (WAXD) unit with Cu K α radiation source (wavelength λ =0.1542 nm). The sample to detector distance was 125 mm. The beam time exposure was 2 hours for each sample.

Morphology characterizations were conducted by atomic force microscopy (AFM). The tape was embedded in Loctite Heavy Duty Epoxy and cured for 24 hours at room temperature. The embedded tape was cut along the extrusion direction at -120°C by glass knife in microtome (Leica EM UC7 ultramircrotome) unit with a cryo-chamber. The AFM images were collected by a scanning probe microscope (Digital Instruments Nanoscope IIIa) with rectangular type tapping mode probe. The tip radius of the probe was 10 nm. The spring constant was 50 N/m and the resonance frequency was 320 kHz.

2.3. Results and Discussion

2.3.1. Characterization and Properties of Unoriented Tapes

Previously we have described a novel solid state structure of the 50/50 PE/PP system which resulted from a unique surface generating co-extrusion methodology shown in Figure 2.1. This co-extrusion design was previously used to create two component battery separators [11] and other novel micro/nano fiber systems [13]. These polymer systems were processed by taking advantage of the adhesive properties between incompatible polymers such as Surlyn/polystyrene, polyamide 6/polyethylene terephthalate and polyethylene/polypropylene. In all these cases delamination was achieved into micro/nano fibrillar structures by either solvent extraction of one of the phases or by an impinging water jet.

The co-extrusion process produced a uniquely structured PP and HDPE tape which comprises a cross sectional matrix of 8192 x 32 or 262,144 individual PP and HDPE domains. The extrusion or flow direction incorporates semi-continuous domains that are fiber-like. Three different tapes were produced in this study. In addition to the 50/50 PP/HDPE blended tapes as described comprising approximately 263,000 distinct PP and HDPE domains in the extrusion direction, two control tapes comprising PP and HDPE, respectively, were produced by utilizing the same multilayer co-extrusion process.

2.3.1.1. Morphology

The AFM images shown in Figure 2.2 (a, b, c) are as-extruded tapes containing 50/50 PP/HDPE. These unique images show elongated domains in the extrusion direction. The lighter image is PP and the darker image is HDPE. The individual domain width varies considerably between 200 and 500 nm. The white line drawn in Figure 2.2 (c) sketches the rough boundary between PE and PP indicating a large surface contact area and suggesting strong interactions

between the crystals of both phases. Jorden et. Al. [14] previously proposed similar interactions as "entangled crystals" depending on the grade of polymer used in their study. Furthermore, epitaxy between PE and PP is also conceivable [3-5] since both polymers crystallize at a similar temperature.

Further examination of the AFM images in Figure 2.2 indicated that in the individual PP/HDPE domains numerous lamellar are observed perpendicular to the extrusion direction.

2.3.1.2. DSC and WAXD Characterization

The DSC thermographs and WAXD patterns for the PP, HDPE and 50/50 PP/HDPE tapes are shown in Figure 2.3 and Figure 2.4, respectively. These data illustrate that the individual thermal and crystallographic properties of the PP and HDPE components are retained in the coextruded tape indicating the distinct incompatibility of both polymers.

The crystallinity of PP control tape and HDPE control tape were 39% and 63% respectively. In the 50/50 PP/HDPE tape, the crystallinity of PP is 35% and the crystallinity of HDPE is 54%. Compared with the controls, the crystallinity of both PP and HDPE decreased slightly in the 50/50 PP/HDPE tape. As shown in Figure 2.3(b), the crystallization peak of PP control tape is 117°C and the crystallization peak of HDPE control tape is 122 °C. Only one crystallization peak at 120 °C is observed in 50/50 PP/HDPE tape. This indicates that both PP and HDPE crystallize at similar temperature, which could explain 50/50 PP/HDPE tape has slightly lower crystallinity compared with the controls.

As shown in Figure 2.4, WAXS pattern of all undrawn tapes have isotropic ring reflections. PP control tape has six reflections (Figure 2.4(a)) for monoclinic structure: (110), (040), (130) along the hk0 layer line, (022) along the hk2 layer line and two coincidental reflections (041), (111). Two reflections were observed for the orthorhombic structure of HDPE (Figure 2.4(b)), corresponding to (110) and (200) reflections. The combined reflections of PP and HDPE did not change in 50/50 PP/HDPE tape (Figure 2.4(c)), indicating that the individual crystal structures did not change in the blend tape, and that the tape was composed of two distinct phases.

2.3.1.3. Mechanical Properties of Unoriented Tape

The room temperature mechanical properties of the as-extruded PP and HDPE control tapes and the 50/50 PP/HDPE tape were determined in accordance with ASTM D882. The draw rate was 100%/min and all tests were conducted in triplicate. Figure 2.5 illustrates representative stress-strain curves for the three different samples. Average values for the modulus and yield strength for the HDPE control were 0.56 ± 0.02 GPa and 14.4 ± 0.4 MPa, respectively. The modulus and yield strength averages for PP control were 0.75 ± 0.13 GPa and 19.7 ± 0.5 MPa, respectively. The 50/50 PP/HDPE blend had averages for the modulus and yield strength of 0.75 ± 0.07 GPa and 19.3 ± 2.0 MPa, respectively.

These data show that the mechanical properties of the 50/50 PP/HDPE co-extruded tape are similar to the PP control tape and higher than HDPE tape. This re-affirms as shown in the AFM image that the interfaces between PP and HDPE have good adhesion which leads to mechanical synergism between PP and PE.

These results illustrate that a unique multicomponent morphology is produced by utilizing a novel multiplication and co-extrusion process between two incompatible polymer components. This process allows the domain morphology of the tape to be controlled based on the process design. Furthermore, this process allows the ability to produce very small multi-component domain morphologies having an extremely high domain interfacial area.

2.3.2. Orientation of Tapes

It is well known that the solid state orientation of PE and PP into stiff and strong tapes depends on the precursor melt structure and on the cooling and strain rate conditions. The processing conditions to create optimum mechanical properties are dependent on the specific structural characteristics of tape at the end of the processing stage. This implies that a novel approach to create a PP/PE system prior to orientation is needed to achieve desirable properties. Our unoriented tape revealed the previously discussed complex structure showing interpenetration at the interface between the components. This was as a result of the novel extrusion methodology which enable high temperature orientation of tape comprised of two incompatible crystalline polymers.

2.3.2.1. Mechanical Behavior During Orientation

Figure 2.6 (a) and (b) shows the mechanical behavior during orientation of the 50/50 PP/HDPE at 130°C. The data summarized in Table 2.1 follows the definitions in Figure 2.6 of modulus (2% secant), yield stress, work hardening slope, and draw ratio at fracture initiation.

In Table 2.1 it is shown that HDPE cannot be successfully oriented at 110 °C since the work hardening is very small and fracture initiation occurred at a relatively small draw ratio, 12, primarily due to non-uniform deformation (instability) at 110 °C during the orientation process.

Similarly, PP also showed fracture initiation at a low draw ratio, 12x, at 110 °C due to draw instability. The draw temperature (110 °C) is too far removed from the melting point of PP for efficient orientation in the solid state under uniaxial tension. This stress state requires dilation which causes cavitation and subsequently premature failure at low draw ratios.

It was very interesting to note that 50/50 PP/HDPE can be uniformly oriented at 130 °C to a draw ratio of at least 25x with work hardening of 0.3 MPa. This could only be achieved as a result of strong adhesive behavior between PP and HDPE. HDPE control tape could not be oriented successfully at 130°C since this temperature is too close to the melting point of HDPE. While PP could be drawn to a very high draw ratio up to 29x without fracture. Surprisingly, PP/HDPE 50/50 tape could be drawn to draw ratio of 25x with similar work-hardening slop as PP. In the PP/HDPE 50/50 tape, polyethylene could be oriented at near its melting point where considerable work hardening occurs prior to the onset of fracture. This indicates that PP carries along HDPE due to the strong adhesion resulted from the complex co-continuous morphology.

2.3.2.2. Mechanical Behavior of Oriented Tapes at Room Temperature

Tapes oriented at 130°C became the basis for deeper investigation. HDPE was oriented at near its melting point and PP at a desirable orientation temperature where considerable work hardening occurs prior to the onset of fracture. Six different draw ratios (DR) were picked to further investigate the structure-properties relationships of tapes oriented at 130°C: (1) DR = 1.25 at the yield point; (2) DR = 3.4 at the end of necking region and beginning of strain-hardening

region; (3) DR = 8.5 and 14 in the middle of strain-hardening region; (4) DR = 20 at the end of work-hardening region; (5) DR=25 at the maximum draw ratio before fracture.

In Figure 2.7, typical stress-strain curves taken at room temperatures are for 130 °C oriented tapes of various draw ratios. The mechanical properties of these tapes are summarized in Table 2.2. At draw ratio of 25, tapes were produced having a modulus of around 10 GPa, a tensile strength of about 540 MPa and an average strain at break of 10%. A comparison with commercial tapes is made in Table 2.3.

2.3.2.3. Structural Characterization of Oriented Tapes

The DSC curves for five increasing draw ratios are shown in Figure 2.8 (a~e). Up to a draw ratio of 3.4x, which is the end of the necking region, the DSC indicates that significant morphological changes did not occur. However, at a draw ratio of 8.5x, which is in the middle of the work hardening region, two peaks are observed for HDPE at 130 °C and 142 °C and two peaks for PP at 160 °C and 168 °C. Bashir et.al. [15] observed similar melting behavior for oriented polyethylene and related this observation to a detailed discussion of an oriented shish-kebab morphology. A peak at 130°C due to the lamellar material beside peaks at around 140°C and above could indicate the presence of shish-kebab morphology. The endothermic peaks at around 140°C and above indicates the presence of highly chain-extended structures. More recently Mi et.al [16] showed using a novel tape forming procedure that oriented polypropylene was composed of shish-kababs and quantitatively related this morphology to mechanical behavior. It is tempting to suggest that the appearance of two new high temperature melting peaks in both oriented HDPE and PP is

due to a shish-kebab morphology in both polymers resulting from the unique structure of the unoriented tape.

The DSC observations become more complex in the work hardening region shown for draw ratios 14 and 20. In HDPE, the 142°C peak which can be attributed to more chain extension disappears entirely at the draw ratio of 20. This indicates that when HDPE is drawn at 130 °C in the 50/50 PP/HDPE tape, HDPE has sufficiently crystal chain mobility to relax before recrystallization, that is, the more chain extended structure of HDPE folds back again into the thinner lamellar configuration. The crystallinity of HDPE remains constant during orientation while the crystallinity of PP increases almost linearly as draw ratio increase as shown in Fig.9. The two melting peaks from PP increase and sharpen significantly too. The PP continues to form more extended-chain core fibrils as draw ratio increases. Those extended–chain core fibrils act as nuclei for the lamellar crystallization of the rest of PP, thus increase the overall crystallinity of PP.

Wide angle X-ray results in Figure 2.10, show that both HDPE and PP continue to be oriented with increasing draw ratio. Figure 2.11 (a) shows the Herman's orientation functions f_c based on the PP (110) and PP (040) planes. The first indication of considerable orientation is at a draw ratio of 3.4 which is around the beginning of the work hardening region. Reflections of both PP and HDPE get sharper as draw ratio increase. This surprising result indicates that the HDPE is oriented due to its adhesion to PP at 130°C. This suggests the observation that the HDPE is adhered to the PP, and follows the PP orientation during drawing. As expected, considerable orientation occurred in the work hardening region, fc for PP increases from 0.64 to 0.97 from DR 3.4x to DR 25x.

Figure 2.11 (b) shows that both the modulus and the tensile strength increase linearly in the region between draw ratio 3.4 and DR 25. Therefore, comparison with Figure 2.11 (a) shows that the mechanical behavior correlates linearly with the orientation function. The effect of orientation on the mechanical behavior can therefore be broadly described in two regions. At low orientation (draw ratio $1 \sim 3.4$), the increase in the tape modulus and tensile strength is primarily due to further orientation of the hierarchical morphologies in both HDPE and PP shown in Figure 2.2. The WAXD pattern shown in Figure 2.10 (a, b) indicate that considerable orientation occurred between DR 1.25 and 3.4 in both polymers. However, no changes in melting behavior was observed at draw ratio of 3.4x in DSC thermograph (Figure 2.8. (a, b)). The crystallinity of PP only increased slightly when the draw ratio increased from 1.25 to 3.4. This indicate that no extended chain crystals were generated ever though orientation of PP and HDPE crystals occurred. As the draw ratio was increased to 8.5, changes in the crystalline morphology previously described in DSC observations took place in both polymers. The formation of shish-kabab structure of PP in the work hardening region accounts for these important enhancements in both the modulus and tensile strength of these tapes.

2.3.3. Comparison with Other Materials

Compared with previous work of LDPE/PP tape [8] and PA6/PEO tape [9] produced from the same technique, 50/50 PP/HDPE tape has higher modulus and tensile strength. Comparisons are made in Table 2.3. Common commercial PP strapping materials which are extensively used have modulus up to 2.2 GPa and tensile strength of about 300 MPa. The 50/50 PP/HDPE tape drawn to 25x at 130°C have almost 5 times higher modulus and 2 times higher tensile strength than the common commercial PP strapping material. Other PP composites found in the literature produced by other techniques [17, 18] did not have sufficiently improvement in the mechanical properties. By drawing tapes produced from simple melt-mixing of 75wt% HDPE and 25wt% PP, the modulus was improved to 3.5 GPa [17]. This tape also fibrillates prematurely which makes application difficult. All-polypropylene composites [18] produced by co-extrusion of PP with PP co-polymers using complex orientation procedures generate oriented narrow strips of PP with modulus of 3.8 GPa at draw ratio of 25.

The 50/50 PP/HDPE tape described in this paper was produced by a one-step orientation at 130°C. As shown in Figure 2.12., the tape did not fibrillate during orientation due to sufficient adhesion between the incompatible components. The mechanical properties were improved considerably when compared to commercial PP tapes.

2.4. Conclusions

A novel multiplication co-extrusion process was described to produce tapes from incompatible polymers. The unique feature of this process is the creation of extra-large contact area between the two components during extrusion. Stiff and strong tapes were made by combining equal amounts of polyethylene (HDPE) and polypropylene (PP) which are known to be incompatible due to poor adhesion between components.

Particular emphasis in this work was finding optimum processing conditions. Tapes with the optimum mechanical properties were created by orienting at 130°C. These tapes were stiffer and stronger than various commercial tapes and did not fibrillate during orientation. At this temperature, the polyethylene is molten and is oriented by the polypropylene which serves as a template. Also, at this temperature, the polypropylene is oriented in the solid state as evidenced by considerable increase in crystallinity.

AFM analysis of the tape showed a rough boundary between PE and PP indicating the existence of a large surface area between the two components. It was suggested that enhanced adhesion between both components could be as a result of epitaxial crystallization of one component onto the other and since both PE and PP were observed to crystallize around the same temperature.

Upon orientation, the DSC results at various draw ratios showed that each polymer contained two melting peaks. The high melting peak was attributed to chain extension and the low melting peak to chain folding indication the possible existence of a shish-kebab like morphology. Further studies are needed with incompatible crystallizable polymers to confirm these observations.

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	Orientation Temperature ([°] C)	Modulus (2% secant) (MPa)	Yield Stress (MPa)	Work- hardening Slope (MPa)	Fracture Initiation (Draw Ratio)
50/50	110 [°] C	77±12	7.7±1.2	0.3	20.5±1
PP/HDPE	130 [°] C	48± 5	2.8±0.5	0.2	25.5±0.5
	110 [°] C	147±14	9.1±1.4	0.3	12±1
FF	130°C 89±	89±8	4.1±0.3	0.2	29±2
HDPE	110 [°] C	41±4	5.9±0.4	0.1	8±1
	130 [°] C	-	-	-	-

Table 2.1. Analysis of stress-strain during high temperature orientation based on average of three experiments; error bars stand for standard deviation.

Draw Ratio	Modulus (GPa)	Tensile Strength (MPa)	Strain at Break (%)
1.25	0.9 ± 0.1	29 ± 1	1355 ± 70
1.6	1.0 ± 0.1	41 ± 2	929 ± 102
3.4	2.8 ± 0.3	179 ± 2	215 ± 65
8.5	3.5 ± 0.2	238 ± 38	13 ± 2
14	5.5 ± 0.6	321 ± 29	10 ± 1
20	6.6±0.7	410±80	10 ± 2
25	9.8±0.9	538±145	10 ± 3

Table 2.2. Summary of the mechanical properties of oriented 50/50 PP/HDPE tapes. Results arebased on the average of 5 specimens; error bars stand for standard deviation.

Materials	Modulus (GPa)	Tensile Strength (MPa)	Strain at Break (%)
LDPE/PP tape (DR=22) ^[8]	6.1 ± 0.3	370 ± 56	-
PA6/PEO tape (DR=6) ^[9]	4.2 ± 0.1	235 ± 51	8 ± 1
Commercial Floss ^[9]	0.5 ± 0.3	170 ± 3	42
PP/HDPE(25/75) nanocomposite ^[17]	3.5	60	-
All-PP composites ^[18]	3.8	190	-
Commercial PP Strapping Material	2.2 ± 1.1	298 ± 8	50 ± 17
50/50 PP/HDPE Tape DR=25 (Drawn @ 130 [°] C)	9.8±0.9	538±145	10 ± 3

 Table 2.3. Comparison with other materials.



Figure 2.1. Schematic illustration of (a) co-extrusion and multiplication system; (b) theoretical cross-sectional melt structure during different multiplication steps; (c) theoretical tape structure.



5 µm x 5 µm

2 µm x 2 µm



1 µm x 1 µm

Figure 2.2. Morphology of unoriented tapes in side view parallel to extrusion direction characterized by AFM phase images. Domain with lighter colors (higher moduli) are PP; domains with darker colors (lower moduli) are HDPE. Superimposed red dash line (c) highlights the PP-HDPE interface.



Figure 2.3. DSC thermograph of unoriented PP control tape, HDPE control tape, 50/50 tape; (a) heating scan showing melting peaks; (b) cooling scan showing crystallization peaks.



Figure 2.4. Wide angle X-ray diffraction pattern of unoriented (a) PP control tape; (b) HDPE control tape; (b) 50/50 PP/HDPE tape.



Figure 2.5. Typical stress-strain curve of unoriented PP control tape, HDPE control tape, 50/50 tape tested at 100%/min, room temperature (a) overall curve (b) blow-up plot in 0-5% strain range.


Figure 2.6. Stress-strain curve during high temperature orientation of 50/50 PP/HDPE tape at 130°C. (a) is the blow-up plot of (b) in the 0-250% strain range.



Figure 2.7. Typical stress-strain curves of oriented 50/50 PP/HDPE tapes at various draw ratio at room temperature.



Figure 2.8. DSC thermograph of oriented 50/50 PP/HDPE tapes at draw ratio of (a) 1.25; (b) 3.4; (c) 8.5; (d) 14; (e) 20.



Figure 2.9. Crystallinity of PP as a function of draw ratio.



Figure 2.10. Wide angle X-ray diffraction pattern of oriented 50/50 PP/HDPE tapes at draw ratio of (a) 1.25; (b) 3.4; (c) 8.5; (d) 14; (e) 25.



Figure 2.11. (a) Herman's orientation factor as a function of draw ratio; (b) modulus as a function of draw ratio (green) and tensile strength as a function of draw ratio (blue).



Figure 2.12. Photo of Oriented Tapes.

Chapter 3

Fabrication of Surlyn[®] Ionomer Fibers Using a Novel Co-Extrusion Approach and Mechanical Property Characterization

3.1. Introduction

Ionomers intrigues numerous studies due to its morphological structure and unique properties such as self-healing¹ and tunable shape memory ². Based on Eisenberg's definition³, ionomers are defined as polymers in which bulk properties are governed by the ionic aggregates. Neutralized poly (ethylene-co-methacrylic acid), usually known as Surlyn, is one of the most studied ionomer. Based on the chemical composition of Surlyn ionomer, it consists of three major repeat units: the ethylene segments, the un-neutralized methacrylic acid segments and methacrylic acid partially or fully neutralized with a metal cation such as sodium, zinc or lithium. The neutralization results in aggregation of ionic groups, which produce remarkable difference between ionomers and ethylene-co-methacrylic acid copolymers in mechanical and other physical properties⁴.

The morphological structures were discussed intensively by Register⁵, Tadano⁶ and Eisenberg^{3,7} in 1990's. In the multiplet-cluster model raised by Eisenberg⁷, a region of restricted mobility surrounding a multiplet is defined, and the thickness of the restricted mobility layer is postulated to be related with the persistence length of the polymer. The regions of restricted mobility overlap with each other and form contiguous regions as ion content increasing. The multiplet-cluster model for the morphology of random ionomers is well agreement with wide range of phenomena in experiment even though the hypothesis on thickness of the restricted mobility

region is not agreed precisely with molecular simulations⁸. The generally accepted morphology model of ionomers is considered to be composed of three phases: lamellar crystallites, interlamellar amorphous polymeric material and ionic aggregates distributed within the amorphous lamellae⁵. In the differential scanning calorimetric studies, a transition peak other than the melting of lamellar crystallites of ethylene segments appears. Tadano assigned that peak to the order-disorder transition of ionic clusters in ionomer ⁶, while Register et al. assigned that peak to the melting of secondary crystallizes of ethylene. The morphology of the ionomers is still not fully understood yet.

The mechanical properties of ionomers are of key importance to understand the morphological structures because the ionic aggregates associated closely to the mechanical properties ⁹. However, the macroscopic mechanical properties of the ionomers, i.e. the tensile modulus and tensile strength, have not been discussed in great details yet, especially in fiber form. There are only a few examples of ionomer fibers, in which fabricate ionomer fibers via melt blowing with limited characterization information. It is interesting to study the ionomer fibers, either alone or in composites, in part because of several potential applications envisioned including gas filtration membranes¹⁰, silver-containing anti-microbial membranes¹¹, porous battery separators with improved wetting¹², and shape-memory materials building on recent work on Surlyn® 8940 films².

Therefore, the mechanical properties of Surlyn fibers were studied in conjunction with thermal analysis in this study. The Surlyn fibers were produced using the co-extrusion and multiplication technique developed by Baer, Wnek et al. ¹⁴, which can produce nano-/micro-fibers with superior mechanical properties over other majority type of fiber production method.

3.2. Experimental

3.2.1. Materials

Surlyn 8940 resin was purchased from DuPont in pellet form. Surlyn® 8940 containing 5.4 mol% methacrylic acid (MA) groups has 30% of their acid groups neutralized¹. Prior to processing, the ionomer was dried in vacuum at 55°C for 24 hours to remove residual moisture. Polystyrene (PS) MC 3650 (PolyOne) was utilized as sacrificial material which functioned as the matrix of Surlyn® fibers. Toluene (Fisher Scientific, HPLC Grade) was used to remove the PS matrices to yield Surlyn® fibers in microns to submicron scale.

3.2.2. Fiber Fabrication and Isolation

The fabrication of Surlyn® fibers contains two steps: (1) processing of as-extruded Surlyn®-PS composite tapes, (2) extraction of PS. In the first step, as-extruded Surlyn®-PS composite tapes were processed by co-extrusion and multiplication process as shown in Figure 3.1. There are n number of vertical multipliers and m numbers of horizontal multipliers. In the process, the PS and Surlyn® were melted in separate extruders and fed into an A/B feedblock with one polymer melts stack horizontally on another. The melt consisting of A/B horizontal layers turned into vertical A/B layers after gone through the first vertical multiplier. In the first vertical multiplier, A/B horizontal melt was cut horizontally in the middle, then the two fields turned 90° in the vertical multiplier and recombined into two-vertical layer melt. This vertical multiplication process was repeated n - 1 times to yield a melt with a 2^n A/B vertical-layered-structure. After n vertical multipliers, PS was fed on the top and bottom of the melt with 2^n A/B vertical-layered structure in the feedblock by a third extruder C. Then the melt with 2^n A/B vertical layers sandwiched between

PS horizontal layer went through m horizontal multiplication. In the horizontal multiplication, the melt was cut in the middle vertically, so that the vertical layers decreased by half every time when melt went through the horizontal layers. The horizontal layer number was doubled after every horizontal multiplication by combining the vertically-cut melt after 90° rotation into horizontal direction. More detailed description of the co-extrusion and multiplication process could be found elsewhere.^{9,10} Finally, as-extruded Surlyn®-PS composite tapes with fiber-in-matrix structure as shown in Figure 3.1(b) were extruded from the exit die and collected by chill roller. The final Surlyn®/PS composts contains 2^{n-m} by 2^m Surlyn® fiber domains. In this case, a total of 13 vertical multipliers and 5 horizontal multipliers were employed, resulting in a tape cross-section comprised of 256 row by 32 column fiber array producing a total of 8,192 Surlyn® rectangular fiber domains embedded in the PS matrix emanating from a 3-inch tape die. In the co-extrusion process, all pumps, feedblocks and multipliers were all set to 225°C where the viscosity of PS and Surlyn® match well with each other. The pump rate was set to A:B:C = 10:10:2.

In the second step, co-extruded Surlyn-PS tapes were immersed in toluene for 24 hours and the tapes were gently compressed to remove excessive toluene, and then allowed to dry over 24 hours in a fume hood. The theoretical mass fraction of Surlyn in the raw tape samples is about 45.5%, although isolated, dried samples were 37% to 42% indicating that some Surlyn was lost in the PS extraction and drying.

3.2.3. Characterization of Surlyn Fibers

The morphology of Surlyn® fibers was studied using JEOL(JEOL-JSM-6510LV) scanning electron microscope (SEM) for capturing SEM images. A TA Instruments Q2000 differential scanning calorimetry (DSC) was employed with a scan rate of 5°C/min.

Mechanical properties were measured room temperature at 10%/min, 100%/min, 500%/min and 1000%/min strain rate using an Instron 5965 tensile testing machine to study the effect of strain rate on mechanical properties. An MTS Alliance RT/30 was used to draw Surlyn® fibers to 300% strain at room temperature, and at 60°C and 80°C. The mechanical properties of all oriented Surlyn fibers were tested in room temperature at 100%/min strain 24h after orientation to eliminate the effect of aging by keeping the aging time constant.

3.2.4. Annealing

Surlyn fibers were oriented to 300% strain at 60°C, 1000%/min strain rate in MTS heating chamber and then kept for 1hr or 2hrs in a heating chamber with fixed strain against shrinkage.

3.3 Results and Discussion

3.3.1. Characterization of Surlyn® Fibers from Surlyn®/PS As-extruded tapes

The as-extruded Surlyn®/PS tapes were washed in toluene after the co-extrusion process to isolate 3-inch tape die fiber bundles. SEM images of such fibers are shown in Figure 3.2. Individual fibers are rectangular in shape as expected have average dimensions of about 1 by 3 μ m (fiber thickness by fiber width). A DSC trace of washed and dried fibers (Figure 3.3) shows two endotherms at 66°C and 91°C. Using the nomenclature of Wakabayashi and Register,¹³ the peak at ca. 45-50°C (T_{m2}) is attributed to melting of small (secondary) polyethylene-rich crystallites, and known to be sensitive to the thermal history of such ionomers. The second peak at ca. 90°C (T_{m1}) is attributed to melting of primary, polyethylene segment-rich crystals.

The mechanical properties of 3-inch tape die Surlyn fibers were assessed at different strain rates and typical results are shown in Figure 3.4. The tape die fiber stress-strain curves were observed to be, in general, remarkably similar to raw Surlyn® 8940 film. For example, commercial Surlyn® 8940 film exhibits tensile strains at room temperature of up to 1000% with yield strengths around 20 MPa and ultimate tensile strengths at break of about 40 MPa and stress-strain curve contours¹ similar to those shown in Figure 3.4. The overall profile of stress-strain curves does not change with the strain rate during tensile test. Surlyn fibers exhibit continues necking plateau after reaching maximum yield strength with slightly strain-hardening until ~300% strain. After ~300% strain, a further strain-hardening takes place and Surlyn® fibers start to break. A significant series of fluctuations appears during the second strain-hardening process, indicating some degree of fiber fracture. With increasing strain rate, both the modulus and yield strength show an overall small increase. The results are summarized in Table 3.1.

3.3.2. Effect of drawing

In an effort to enhance the tensile properties of Surlyn® fibers, the effect of drawing was studied. Based on many tensile test results on Surlyn® fibers at room temperature, a final strain of 300% before the necking plateau (draw ratio of 4) was chosen to avoid fiber breakage. Thus, Surlyn® fibers were oriented at 100%/min, 500%/min and 1000%/min strain rate to a final strain of 300% in room temperature. The Surlyn® fibers with a draw ratio of 4 were then tested at 100%/min in room temperature. As shown in Figure 3.5 (a), both tensile strength and modulus increase with increasing strain rate during drawing. When drawn at 1000%/min at room temperature, samples achieved modulus of about 257 MPa and tensile strength of 57 MPa.

DSC traces (Figure 3.5b) indicate that T_{m2} decreased from 66 °C to ca. 45°C (compare with Figure 3.3) with no apparent change of T_{m2} and Tm1 with strain rate. The downward shift of T_{m2} maybe due to an overall reduction of the sizes of secondary polyethylene-rich crystallites upon drawing, and/or from the creation of different populations and sizes of polyethylene-rich regions as the result of drawing.

In an attempt to further enhance the tensile properties of Surlyn® fibers, drawing was also conducted at higher temperatures. The temperatures were chosen before the melting of first and secondary polyethylene crystallites respectively at 80°C and 60°C. For appropriate comparisons to drawing conditions at room temperature, Surlyn® fibers were stretched to draw ratio of 4 at 1000%/min strain rate at 60 °C and 80 °C. The mechanical properties of the oriented Surlyn® fibers were tested at room temperature and 100%/min strain rate 24 hours after orientation. The results are as shown in Figure 3.6 (a). The moduli of fiber bundles drawn at 60° C and 80° C are 271 ± 21 MPa and 257 ± 49 respectively, a relatively insignificant increase compared with the fibers drawn at room temperature as summarized in Table 3.2. The tensile strengths of fibers oriented at 60°C and 80°C are 71 \pm 28 MPa and 69 \pm 27 respectively, which are ca. 25% higher than the fibers drawn at room temperature. Drawing conditions might be further optimized, especially between 60°C and 80°C, to afford additional improvement of the modulus and tensile strength. DSC thermographs in Figure 3.6 (b) shows that T_{m1} did not change after drawing at 60°C and 80°C. The T_{m2} of fibers drawn at 60°C and 80°C decrease to 49°C and 47°C respectively, similar to samples drawn at room temperature.

3.3.3. Effect of annealing

As suggested in the literature, an annealing process could contribute significantly to the bulk

modulus of an ionomer^{9,13} Thus, fiber bundles were annealed in the MTS heating chamber after being drawn to 300% with fixed strain for different durations. The annealed fibers were tested at room temperature at 100%/min strain rate, 24h after the annealing process. The test results are shown in Figure 3.7 (a) and summarized in Table 3.3. After annealing for 1h, the modulus and tensile strength increased to 352 MPa and 77 MPa, respectively. Fibers drawn at 60°C and subsequently annealed at 60oC for 2 hours have moduli in excess of 350 MPa and tensile strengths in excess of 70 MPa. We suggest the following interpretation for the significant property improvement.

As noted earlier, a DSC trace for Surlyn® 8940 fibers after toluene extraction and drying (Figure 3.3) indicates the presence of two peaks ascribed to T_{m2} and T_{m1} . However, drawing at 60°C and annealing for 2 hours at 60°C diminishes the original T_{m2} DSC peak and leads to growth of a 'new' peak at ca. 70°C (Figure 3.7 b). It is known¹³ that annealing of ethylene/methacrylic acid ionomers can raise T_{m2} up to as high as ca. 80°C, suggesting that the 70°C peak in Figure 3.7 b is a new T_{m2} , possibly resulting from larger and better developed secondary crystallites that were formed at the expense of the original, lower Tm2 species. Also, it has been proposed^{9,13} that crystallites (especially secondary crystallites) and the ion-rich clusters can work in concert to maximize mechanical properties of these ionomers, which is perhaps why the mechanical properties of Surlyn® fibers show improvement with annealing after drawing, and also perhaps why drawing of fibers at $80^{\circ C}$, above T_{m2} , is not effective in further enhancing mechanical properties. There likely a complex time-temperature dependence regarding annealing conditions, as evidenced by samples annealed at 60°C for 24 h which exhibit the greatest modulus of 480 MPa but an inferior tensile strength of 56 MPa compared to samples annealed at 60°C for 2 h. While we have not optimized the draw/anneal time and temperature space, moduli in excess of 350 MPa

and tensile strengths in excess of 70 MPa achieved with a 2-hour annealing at 60°C are quite attractive for many potential applications.

3.4. Conclusions

The present study illustrates the production of Surlyn® ionomer microfibers materials using a novel processing technique. The continuous co-extrusion of Surlyn® fibers within a polystyrene matrix through a tape die followed by the solvent extraction of the polystyrene is a unique method for producing a bundle containing thousands of independent Surlyn® fibers. These co-extruded rectangular fibers show good overall mechanical properties, having a Young's modulus of 236 MPa and an average yield strength of 12.7MPa. After stretching to a draw ratio of 4 and annealing at 60°C for 2 hours, Surlyn fibers achieved a modulus of 378 MPa and a tensile strength of 96 MPa, a significant improvement over un-annealed samples. Drawing to a higher modulus, along with further experiments with different ionomer nanofiber systems and optimization of processing variables, may prove to be a fruitful area for research.

3.5. References

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Strain rate (%/min)	Modulus (MPa)	Yield Strength (MPa)
10	207 ± 10	9.4 ± 0.2
100	215 ± 25	9.6 ± 1.2
500	216 ± 14	12.2 ± 1.2
1000	236 ± 14	12.7 ± 1.3

Table 3.1. Tensile properties of Surlyn fibers tested at different strain rate in room temperature.

*The values are the mean value based on 5 measurements. The numbers after "±" stand for the standard deviation of the mean value.

Orientation Conditions	RT at 100%/min	RT at 500%/min	RT at 1000%/min	60°C at 1000%/min	80°C at 1000%/min
Modulus (MPa)	249 ± 16	252 ± 34	257 ± 19	271 ± 21	257 ± 49
Tensile Strength(MPa)	38 ± 9	40 ± 16	57 ± 4	71 ± 28	69 ± 27

Table 3.2. Tensile properties of Surlyn fibers with a draw ratio of 4, oriented at different conditions.

*The values are the mean value based on 5 measurements. The numbers after " \pm " stand for the standard deviation of the mean value.

Annealing duration	Modulus (MPa)	Tensile Strength (MPa)
1 h	351 ± 17	77 ± 19
2 h	378 ± 33	96 ± 18
24 h	480 ± 81	56 ± 5

Table 3.3. Tensile properties of Surlyn fibers (DR=4, oriented at 60°C, 1000%/min)	annealed for
different times.	

*The values are the mean value based on 5 measurements. The numbers after "±" stand for the standard deviation of the mean value.



Figure 3.1. Schematic drawing of (a) co-extrusion and multiplication process for producing asextruded Surlyn-PS composite tapes; (b) the as-extruded Surlyn-PS composite tape structure. Note that only part of the structure is shown in the figure and the dimensions were exaggerated to show the structure.



Figure 3.2. SEM image of tape die co-extruded, toluene washed Surlyn® fibers. (a) (b) in side view; (c) (d) top view.



Figure 3.3. DSC Thermograph of toluene washed Surlyn fibers first heating cycle.



Figure 3.4. Stress-strain curve of Surlyn fibers tested at different strain rate in room temperature.



Figure 3.5. (a) Tensile properties (b) DSC thermographs of Surlyn fibers oriented to 300% under 100, 500, 1000%/min strain rate at room temperature; tensile tests were conducted at room temperature under 100%/min strain rate; DSC heating rate: 5°C/min.



Figure 3.6. (a) Tensile properties; (b) DSC thermographs of Surlyn fibers oriented to DR=4 at 1000%/min strain rate in different temperatures; tensile tests were conducted at room temperature at 100%/min strain rate; DSC heating rate: 5°C/min.



Figure 3.7. (a) Tensile properties (b) DSC thermographs of Surlyn fibers oriented to DR=4 at 1000%/min, 60°C and then annealed at 60°C with fixed strain for 1h, 2h and 24h; tensile tests were conducted at room temperature under 100%/min strain rate; DSC heating rate: 5° C/min.

APPENDIX:

Future Work Recommendations

Chapter 1: Alkaline Battery Separators with High Electrolyte Absorption from Forced Assembly Co-Extruded Composite Tapes

- 1. Life time of coin cells made from PP/HDPE, PP/PA6 and commercial separators should be measured to further confirm the effect of KOH uptake on battery performance.
- 2. Heat and pressure treatment on PP/HDPE and PP/PA6 separators should be studied to reduce the thickness of separators.
- 3. The mechanical properties should be further studied by optimizing the orientation conditions of precursor composite tapes.
- 4. The stability of PA6 in 6M KOH solution should be tested by analyzing the electrolyte component in the coin cell after life time measurement.

Chapter 2: Oriented Tapes of Incompatible Polymers Using a Novel Multiplication

Co-Extrusion Process

- Study the adhesion between PP and HDPE by changing the "synthetic history" of PE and PP (i.e., site specific metallocene or heterogeneous Ziegler-Natta catalyzed).
- 2. Selection of polyethylene and polypropylene to study the effect of molar mass and molecular weight distribution on mechanical properties.
- Study the AFM phase image of oriented 50/50 PP/HDPE tapes to see if the morphology retained in the oriented tapes.
- Study the mechanism of orientation further by conducting in-situ small and wide angle Xray scattering.
- 5. Change the number of multipliers to study the effect of processing history on morphology and mechanical properties.

Chapter 3: Fabrication of Surlyn[®] Ionomer Fibers Using a Novel Co-Extrusion Approach and Mechanical Property Characterization

 Fabricate Surlyn fibers from poly (ethylene-co-methacrylic acid) ionomers neutralized by different cations.

- 2. Optimize the orientation and annealing conditions of the Surlyn fibers to achieve higher modulus and tensile strength.
- 3. Optimize processing variables such as number of multipliers and processing temperature.
- 4. Study the structural and morphological changes of Surlyn ionomer after orientation and annealing.

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