Contents lists available at ScienceDirect

Materials Today Communications

Effect of annealing temperature on pore formation in preparation of advanced polyethylene battery separator membranes

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ARTICLE INFO

ABSTRACT

Polymeric separator membranes are a key component in modern lithium ion batteries, as they are placed between anode and cathode to prevent short-circuiting while at the same time allowing an efficient diffusion of Li ions. Manufacturing conditions must be finely tuned to reach the many diverse and conflicting requirements for battery separators used in modern consumer applications as well as in electric vehicles. Little has been published about these proprietary combined extrusion/biaxial stretching processes. This work presents a closer look on one of the key aspects of separator membrane formation. Extruded sheets of high density polyethylene containing a hydrocarbon solvent as plasticizer were stretched in machine direction and annealed at temperatures between 100 °C and 120 °C, i.e., in a range between the onset of melting and actual melting temperature, as deduced from differential scanning calorimetry. The formation of stacked-lamellar morphologies as seen in scanning electron microscopy required a minimum strain and was also influenced by processing temperatures. The increase of the annealing temperature led to a significant increase in crystallinity and chain orientation as revealed by texture analysis, performed using X-ray powder diffraction studies on samples after dedicated preparation. After a second stretching step in transversal direction, a clear correlation to separator membrane permeability and porosity was found, with a higher crystallinity leading to lower Gurley values, i.e. higher permeabilities. The effects of blending high density with ultra-high molecular weight polyethylene of different molecular weight onto structure and morphology were also elucidated in detail. In light of the growing market of electric vehicles, high performance and safety are the main focus during separator production. The influence of important production parameters on final membrane properties is discussed.

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1. Introduction

The development and commercialization of secondary lithium ion batteries (LIB) by Sony in 1991 has led to their widespread application in consumer handheld devices including cell phones, camcorders and notebooks [1–3]. While the performance of LIB is an important factor for meeting the energy demand of future generations, battery cell safety, especially in electrical vehicle (EV) and stationary applications, is of great interest for current LIBs [4,5]. In that regard the separator membrane plays an important role in the battery cell. Situated between anode and cathode, the separator is necessary to prevent the contact of the electrodes and a subsequent short-circuiting of the cell while still enabling a sufficient flow of Li ions [6–9]. The review by Arora and Zhang gives a comprehensive overview of separator membrane technology and related film properties [6]. The typical thickness of a separator membrane ranges between 12 and 20 μm, with market demanding thicknesses of 10 μm or even lower. A high porosity in the range of 40–70% is required for a separator to permit a sufficiently fast Li ion diffusion. While porosity alone is not necessarily a good indicator for ionic conductivity (e.g., a dense layer within the separator membrane may block ion transport even at high overall porosities), the Gurley value is typically used as an approximate indicator for ion conductivity. The Gurley value is a measure of air permeability in terms of time needed for $100\,cm^3$ of air to pass through the membrane at a constant pressure of 1.22 kPa and a constant membrane area of $5.07\,cm^2$. Commercial separators reach values as low as 300–400 s [6–8].

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Table 1
Sample compositions.

Composition	Polymer 1 (HDPE)	Polymer 2 (UHMWPE)	Solvent Content	Molecular weight M_W Polymer 1/Polymer 2
A	50% Alathon L5906	–	50%	300 kg/mol
B	17.5% Sunfine SH800	17.5% GUR4012	65%	300/1800 kg/mol
C	17.5% Sunfine SH800	17.5% GUR2122	65%	300/5000 kg/mol

State-of-the-art materials used for separators are polyethylene ("high density": HDPE; "ultra high molecular weight": UHMWPE) and polypropylene. The preparation of porous membranes from polyolefines can in general be done by sintering of polymer powders, by extrusion of polymer melt and mechanical stretching, or by casting or extrusion of polymer solution followed by thermally induced phase separation (TIPS) [10–12]. The latter two methods lead to membranes with barrier pores in the sub-μm region, which is also the target for battery separators. The industrial production of polymeric battery separators is based on melt extrusion and employs mono- or biaxial sequential or simultaneous stretching. In order to meet the requirements for mechanical integrity at lower thicknesses, HDPE is increasingly substituted by UHMWPE. Major processes on the market are the "wet" process (Asahi Kasei, Toray) in which the polymer is processed with a high-boiling paraffinic solvent that is washed out after biaxial stretching of the extruded and cooled film thus generating a porous structure, and the "dry" process (Celgard), in which the pores are formed exclusively due to consecutive monoaxial stretching and annealing steps of the film obtained from the polymer melt [6–9].

During stretching of the extruded sheet-like materials, the polymer chains and crystalline phase are deformed plastically and oriented along the stretching direction [13,14]. In a sequential biaxial process, first a stretching step in machine direction (MD) is applied, followed by a second stretching step in transverse direction (TD). Typically, after each stretching step, annealing is applied to thermally fix the molecular structure by allowing the oriented chains to relax and consequently reduce build-up stress in the material. During the plastic deformation the crystalline phase undergoes a change from a spherulitic to a stacked lamellar or "shish-kebab" morphology [15–18]. This so called flow-induced crystallization is possible due to multiple elongated chains packing together, thus forming nuclei for further lateral growth of crystal blocks (kebab) around this central core (shish). This mechanism is dependent on four major parameters: shear rate, strain, molecular weight of the polymer and temperature. For crystallization to occur, a certain critical strain of the molecular chains is required. Because the extension of chains is counteracted by polymer relaxation, the shear rate needs to be high enough to maintain and propagate further extension. Molecular weight and molecular weight distribution play an important role, with longer chains needing more time for relaxation due to their increased size/weight. Therefore, the higher molecular weight fraction of a given molecular weight distribution is more readily extended, and a certain critical molecular weight is required for flow-induced crystallization at a given shear rate and strain. With increasing shear rate, the critical molecular weight can be reduced to some extent. The effect of temperature is tied to movement and relaxation phenomena of macromolecular chains, with increased temperature leading to reduced relaxation times. Nonetheless, flow-induced crystallization can also occur above the melting point of a given polymer, when shear stress and molecular weight are sufficiently high [15–20].

This work aims to investigate the effect of the annealing temperature during the MD stretching step on the orientation and crystal morphology as well as final separator membrane structure and performance in terms of porosity and Gurley value. Extruded sheets of polyethylene containing a hydrocarbon solvent as plasticizer were MD stretched and annealed at different temperatures ranging between 90 and 120 °C and analyzed by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and X-ray powder diffraction (XRD), including texture analysis. After TD stretching of these precursor films at constant conditions, porosity and Gurley values were determined. By also using different polyethylene blends, effects of polymer material (molecular weight) in combination with key processing parameters were elucidated and discussed in detail.

2. Experimental

2.1. Materials

Granular high-density polyethylene (HDPE) Alathon L5906 supplied by LyondellBasell was used. Alathon L5906 had a nominal molecular weight of 300 kg/mol and a density of 960 kg/m³. The melting point T_m was given as 138 °C. A second powdered HDPE, Sunfine SH800 supplied by Asahi Kasei as well as two ultrahigh molecular weight polyethylene (UHMWPE) grades, GUR4012 and GUR2122 supplied by Celanese, were also used as materials for the preparation of extruded sheets. Sunfine SH800 had a nominal molecular weight of 300 kg/mol and a density of 955 kg/m³. GUR4012 and GUR2122 had nominal molecular weights of 1800 kg/mol and 5000 kg/mol, respectively. A dearomatized aliphatic hydrocarbon mixture with a boiling point in the range of 180–220 °C was supplied by Staub & Co.—Silbermann, Germany, and used as a plasticizer during extrusion and stretching.

2.2. Film and membrane preparation

A twin-screw extrusion system was used for the production of cast films of about 400 μm thickness and 290 mm width according to patent US2013029126 [21]. Three compositions were used as detailed in Table 1. Composition A contained 50% of solvent and 50% of Alathon L5906 while composition B and C contained each 65% of solvent and 35% of a 50:50 blend of Sunfine SH800 with GUR4012 or GUR2122, respectively. The additional solvent content for UHMWPE blends was necessary to achieve stable extrusion conditions due to the increased viscosity of the UHMWPE materials.

A KARO IV stretching device from Brückner was used for both MD and TD stretching steps. MD stretching was done with samples cut from the center of the cast film roll sized 90 × 120 mm (MD × TD). During stretching the sample was covered on both sides by an additional PET film of 200 μm thickness of the same size to prevent early solvent evaporation. Both PET films were stretched together with the sample to ensure a good seal of the sample surface. The polyethylene samples were stretched to a ratio of 5.5 (equal to a strain of 450%) at a strain rate of 100%/s. MD stretching and annealing temperatures were set between 90 and 120 °C with an annealing duration of 30 s. After annealing, the PET covers were removed, leaving a MD stretched sample retaining most of its solvent.

TD stretching was done by cutting a new sample of 120 mm length (along MD) and 90 mm width (along TD) from the center of the MD stretched sample and stretching it to a ratio of 5.5 in transverse direction at 50%/s to a strain of 450%. The stretching temperature was set to 70 °C while annealing was set to a temper-