Influence of rheology and surface properties on morphology of nanofibers derived from islands-in-the-sea meltblown nonwovens

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ABSTRACT

Melt blowing is the most common technique to directly produce nonwovens from polymeric resins without any demand for extra bonding steps. The relatively low diameter of meltblown fibers, $1–2\,\mu m$, makes them superior in separations performance to the competing melt processing technique, spunbonding. To further decrease meltblown fiber diameter, the islands-in-the-sea approach was investigated in this study. Immiscible blends of a water-soluble polymer, sulfonated poly(ethylene terephthalate) (SP), and hydrophilic polybutylene terephthalate (PBT) and hydrophobic polyvinylidene fluoride (PVDF) were meltblown and the SP washed away to produce nanofibers of less than 200 nm diameter. Despite a significant increase in blend drop size upon increasing the minor phase fraction, ϕ, the nanofiber diameter increased only slightly. Thus, we conjecture that nanofiber diameter is mainly controlled by fiber pinch-off, induced by quick stretching during the melt blowing process, rather than being affected by initial drop size. At a high shear viscosity ratio, $\eta_{minor}/\eta_{matrix} > 3$, nanofibers showed a higher level of irregularities, particularly when the polymer flow rate decreased. At $\phi \geq 0.2$ fiber bundling was observed but with nanofibers from PVDF, due to its lower surface energy, compared with PBT, bundling decreased. Our work shows that using polymers with relatively low surface energy, and thus low tendency for coalescence, coupled with low viscosity can result in nonwoven mats of fibers with very low average diameter, low bundling, and an acceptable fiber regularity. With PVDF we achieved a record low average diameter of 36 nm. By using a water-soluble polymer matrix, such as sulfonated poly(ethylene terephthalate), concerns about cost and environmental problems related to chemical solvents are alleviated.

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1. Introduction

Nonwoven mats have broad applications from durables, like filtration devices, protective garments, home furnishing, and agricultural applications, to disposables used in hygienic and medical applications [1]. Polymeric nonwovens, due to their high production rate, low processing costs, and low labor requirement, are growing rapidly [1,2]. According to INDA, worldwide production grew from about 2.6 million tons in 1996, worth about $10 billion, to around 8.9 million tons in 2014, worth $35.6 billion, and is predicted to reach to 12.4 million tons by 2020 [3,4].

In melt blowing molten polymer is extruded into a hot air jet through a die. Hot air draws the polymer, rapidly decreasing its diameter. At the same time, the entrained ambient air decreases the temperature of the molten fibers. Thus, the formation of the fiber occurs between the melt extrusion temperature and its solidification temperature (crystallization temperature, T_c, or glass transition temperature, T_g) [5–7]. Since the fibers are blown by hot air they are still molten and can self-bond to each other on the collecting belt, reducing demand for a further bonding step, which is needed for other melt processing techniques of nonwovens, like spunbonding. Melt blowing produces randomly oriented [6,8–11] and thin $(1–2\,\mu m)$ fibers. These features favor filtration applications [5,7,12,13]. Its high specific surface area results in filtration efficiency for tiny particles from gas or liquid flow. On the other hand, only polymers that have a reasonably low melt viscosity can be blown [1,7].

Melt blowing was originally invented by Wente in 1954 [14–16]. Exxon engineers made this technology commercial [1,17], and since the 1960s this slot type of design has remained the major concept in patented melt blowing dies [18–22]. Research has shown that parameters like geometry of the die, air flow behavior, temperature,

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and die to collector distance, along with viscosity and elasticity of materials can affect the flow field of the process and the formation of meltblown fibers [5,6,10–13].

Nanofibers can be generated from a blend of immiscible polymers, in order to create an island-in-the-sea morphology in the fiber. It is based on the concept that spherical dispersed particles become thin fibrillar species upon applying shear and elongation flows on the blend [23,24]. This approach has been used with melt spinning [25] and spunbonding [2,26,27]. Our research group applied this idea in melt blowing of immiscible polymer blends [28–30]. After the dissolution of the continuous phase of the meltblown microfibers, the islands-in-the-sea (INS) nanofibers form a nonwoven mat with high surface area and small pores. These can provide a higher efficiency, particularly for ultra-fine filtration applications, like separation of water droplets from oil. By using a water soluble polymeric matrix component, the problem of employing an expensive solvent and its environmental issues are alleviated as well [29]. Sulfopolyesters have relatively good thermal stability [31] and were found a good choice for producing INS nanofibers at elevated temperatures, which is required for polymers like polybutylene terephthalate (PBT).

In this work we extend our initial studies to understand how to control the size and quality of the nanofibers produced from meltblown immiscible polymer blends. We found that viscosity ratio, surface energy and interfacial tension between blend components controlled the morphology of the blends, and the resulting islands-in-the-sea nanofibers. We found that from a blend of polyvinylidene fluoride in a water-soluble sulfopolyester matrix we could produce 36 nm nanofibers relatively free of bundling. Such nanofiber nonwovens with various surface properties, and different levels of wettability [32,33] can potentially promote selective separation and filtration [34]. Thus, they can be used for purpose directed filtration applications, like lube oil and diesel filtration.

2. Experimental

2.1. Materials

PBT (Valox 176, SABIC), polystyrene (PS) (9003 53 6, Cat. No. 43011-0, Melt Index:14, Sigma Aldrich), sulfopolyester (SP) (AQ48, Eastman Chemical), and two grades of polyvinylidene fluoride, PVDF1 (Cat. No. 15190, Polysciences Inc.), and PVDF2 (Cat. No. 427152, Sigma-Aldrich) were used in this study. Molecular weights of PS and PVDF were measured by size exclusion chromatography (SEC) using tetrahydrofuran (THF) and dimethylformamide (DMF), respectively, as the carrier solvents at room temperature (Thermo Separation Products Spectra Systems, Waters 2410 RI detector).

Thermophysical properties of the materials were characterized using differential scanning calorimetry (DSC) (TA Instrument Q1000 and Discovery) and thermogravimetric analysis (TGA) (TA Instrument Q500). For DSC analysis a standard run sequence of heating-cooling-heating was used from -80 °C to 250 °C with a heating rate of 10 °C/min, where T_g and T_m were measured during the second heating ramp (Table 1). Also, TGA heated at 10 °C/min under a nitrogen atmosphere was conducted on our materials to assure of their thermal stability at a processing temperature of 265 °C. All samples were dried for 48 h at 40 °C in a vacuum oven to remove the moisture prior to thermo-physical and rheological characterizations, melt processing, and melt blowing experiments.

2.2. Rheological characterization

Rheological properties of pure materials and blends were measure using a strain-controlled ARES G2 rheometer equipped with 25 mm parallel plates with a gap of about 1 mm. In order to determine the linear viscoelastic regions of the materials, dynamic strain sweeps were initially conducted. Dynamic frequency sweeps were employed within the linear viscoelastic region of materials to measure the storage (G′) and loss (G″) moduli, as well as complex viscosity (η^*) as a function of frequency ($1 \leq \omega \leq 400$ rad/s) at 265 °C.

2.3. Interfacial tension measurement

For measuring the interfacial tension blends were prepared in a 5 ml twin screw micro-compounder (Xplore, Netherlands) at 265 °C for 8 min, with the screws rotating at 100 rpm, and under a nitrogen atmosphere [35]. Interfacial tension was calculated from drop diameters and interfacial relaxation found by fitting the Palierne model to dynamic moduli measurements.

2.4. Melt blowing

Blends of PBT/PS, PBT/SP, PVDF1/SP, and PVDF2/SP, needed for melt blowing were made in a Haake batch compounder (Thermo Scientific) at 265 °C, unless otherwise mentioned, with roller blades rotating at 100 rpm for 8 min, after which the blends were immediately quenched with liquid nitrogen (LN2), to freeze their morphology.

The melt blowing process was conducted in a lab-scale apparatus [5,12], built on a conventional capillary rheometer. A piston forces the hot thermoplastic melt into a melt blowing die with five 0.2 mm diameter orifices. Its design mimics in cross section that of typical industrial dies with high throughput [29]. Using a stainless-steel screen, mounted on a rotating drum located 35 cm below the melt blowing die, the fibers were collected on a mesh of spunbound PBT (Cummins Filtration). The temperatures of the melt blowing apparatus and blowing air were set at 265 °C, and the polymer flow rate was set at ~0.2 g/min hole, equivalent to the piston speed of 0.1 mm/s. Hot air pressure at die exit was set at 6 psi (0.5 atm). These values are typical of industrial operation [36]. In order to minimize agglomeration in the blends, melt blowing was begun as soon as the temperature reached 265 °C (heating required about 10 min) [28]. A fan pulls air through the fiber collector, so broken and loose fibers (flies) are removed from the collector and are captured by a filter covered with a layer of spunbond. If the flies are not collected, they could deposit on the fiber collector, causing nonwoven defects [6].

2.5. Extraction of Island nanofibers

Small samples were cut with a scissors from the continuous fiber mats and soaked in appropriate solvents. Solvents were exchanged three times, 2 h each, to dissolve the "sea," the continuous phase and extract the "island" nanofibers. Toluene at room temperature was used to extract fibers; for SP matrices distilled water at 60 °C. The extracted nanofibers were dried in a hood for 24 h.

2.6. Morphological characterization

Polymer blends were cryofractured in LN2. All blends and fibers were surface-coated with 5 nm iridium using a Leica EM ACE600 sputter coater. A scanning electron microscope (SEM) (Hitachi S-4700 and SU-8230) was used to image the samples.

For each blend or fiber mat sample, about 200 drops or fibers were measured using the image analysis software, NIH ImageJ™. Then, Origin Lab by ORIGIN™ was used to fit the drop and fiber distribution data with a lognormal distribution function, to determine geometric average and coefficient of variation (CV) from: