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Existence of microdomain orientation in thermoplastic elastomer through a case study of SEBS electrospun fibers

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ABSTRACT

Although the microdomains of polymeric systems including the thermoplastic elastomers in the as-spun electrospun fiber were reported, the orientation of microdomains has not yet been well clarified. The present work shows an existence of microdomain orientation through a case study of a well-aligned electrospun fibers of polystyrene-block-poly(ethylene-co-1-butene)-block-polystyrene triblock copolymer (SEBS) obtained from an electrospinning unit equipped with a rotational disk fiber-collector. Two-dimensional small-angle X-ray scattering (2D-SAXS) patterns of the as-spun electrospining SEBS fibers show elliptical and four-point patterns suggesting an orientation of distorted and fragmented lamellar microdomains. The electrospun fibers obtained from a low rotational disk collector speed (31.5 m/min) exhibits a significant microdomain distortion whereas the fibers obtained from high take-up velocities (310 m/min, 620 m/min, and 1240 m/min) show higher fragmented-microdomain stretching. By annealing the electrospun fibers, the fibers develop an isotropic SAXS pattern with traces of the remained anisotropic orientation. Based on the above mentioned evidences in SEBS, the present work, for the first time, clarifies that the as-spun thermoplastic elastomers fibers show not just a simple microdomain as used to be observed by transmission electron microscope (TEM) but rather with orientation which can be confirmed by SAXS.

1. Introduction

For decades, the uses of thermoplastic elastomers (TPEs) have been increasing due to advantages of thermoplastic and elastomeric properties related to high strength and toughness. At present, the development of TPEs has reached a certain level where a variety of TPE copolymers are available [1,2]. Polystyrene-b-poly(ethylene-co-1-butene)-b-polystyrene triblock copolymer (SEBS) is one of the earliest developed TPEs and is used in daily-use tools, automotive parts, construction adhesives, and so on, because of their superior weathering resistance resulting from the hydrogenation of unsaturated chemical linkages [3–5]. The SEBS consists of a hard block (polystyrene block, or S block) and a soft block (poly(ethylene-co-butene) block, or EB block). This material is a typical block copolymer with self-aggregation of the internal structure. Since the solubility parameters of these two blocks are significantly different, microphase separation of the S microdomains in the EB matrix is generated, especially when the styrene content is less than 30%.

Up to present, various microphase-separated morphologies of polystyrene based block, mostly in films, have been reported, for example, spherical [6], cylindrical [7,8], and lamellar shape [9]. The morphology of microdomains are found to be depending on several factors, such as polystyrene weight fraction [10], solvent type [11,12], and temperature [13,14], etc. Several examples of TPEs in film form have been reported about microdomain distortion and its orientation including how microdomain induced specific mechanical properties [15,16].

Electrospinning is known as a technique for fabricating ultrafine fiber, ranging from nano- to micro-scale via electric force [17]. In the case of TPEs, electrospinning might be an effective way to utilize an intense stress in a confined geometry to control the microdomain orientation as seen in thermoplastic case. For example, Fong and Reneker reported a small and peculiar shape of phase-separated domain in the electrospun fibers of a polystyrene-b-polybutadiene-b-

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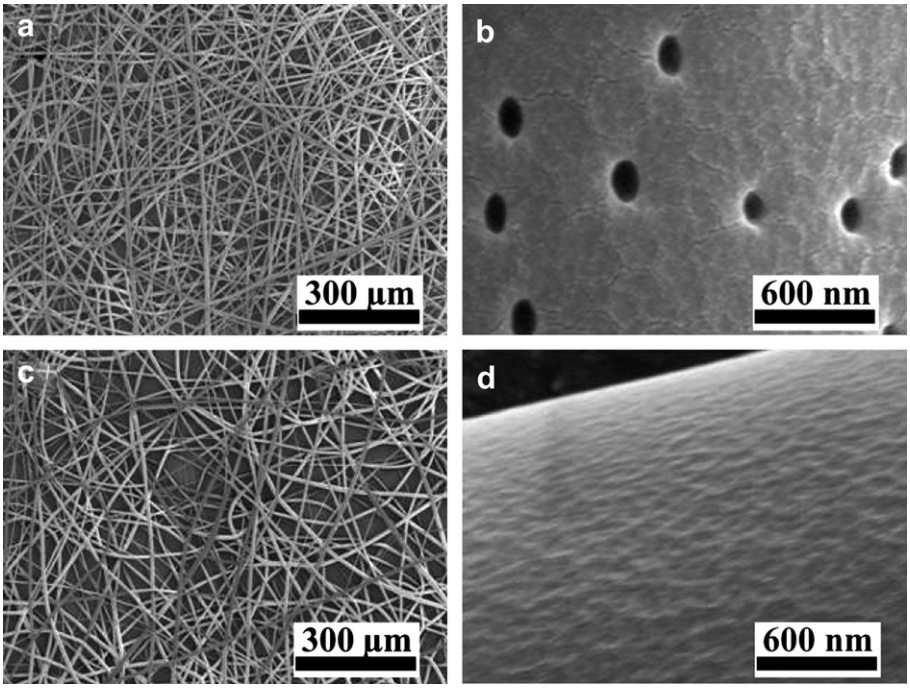

Fig. 1. SEM micrographs of SEBS electrospun microfibers obtained from an accelerating voltage of 20 kV: (a) and (b) under 30% RH; (c) and (d) under 23% RH.

polystyrene triblock copolymer (SBS) due to high evaporation rate of volatile solvents and at that time the polymer chain mobility was limited to end up with a segregation in a thermodynamically non-equilibrated microdomain structure [18]. Ma et al [19]. and Kalra et al., [20], showed the relevant results, especially a small and disordered structure of the microdomains, which were termed as the non-equilibrium state of microphase separation in electrospun TPEs, as evidenced from transmission electron microscope (TEM) images.

Up to present the lamellar microdomains and their orientation of the TPE films have been reported and it seems that the microdomains of the films are similar to those of the fibers. In the case of SEBS film, it was reported that the microdomain orientation of SEBS was due to shear force [21]. For fibers, although electrospinning is a technique that favors the chain alignment to give orientation of the microdomain morphology, to our best knowledge there is no report related to microdomain orientation in the as-spun fiber. Most dealt with the electrospun fibers with irregular microdomain which an annealing and stretching process further develops fiber orientation.

Surprisingly, when we prepared the SEBS fibers by using an electrospinning system equipped with a rotational disk collector which can control the speed of the fiber-collector followed by a careful morphology analysis based on SAXS patterns, we found anisotropic microdomain orientation existed in our SEBS. In other words, the results confirm that there is microdomain orientation in the TPEs fibers. The present work, thus, aims to show an existence of microdomain orientation in TPEs through a case study of electrospun SEBS which the factors involved in microdomain orientation in the fibers such as the control of fiber alignment via an electrospun system equipped with disk collector and the annealing process were also taken in our consideration.

2. Experimental section

2.1. Materials

SEBS triblock copolymer (specification: 32 wt % styrene content, Mw = 80 000 g/mol and Mn = 50 000 g/mol, and melt flow

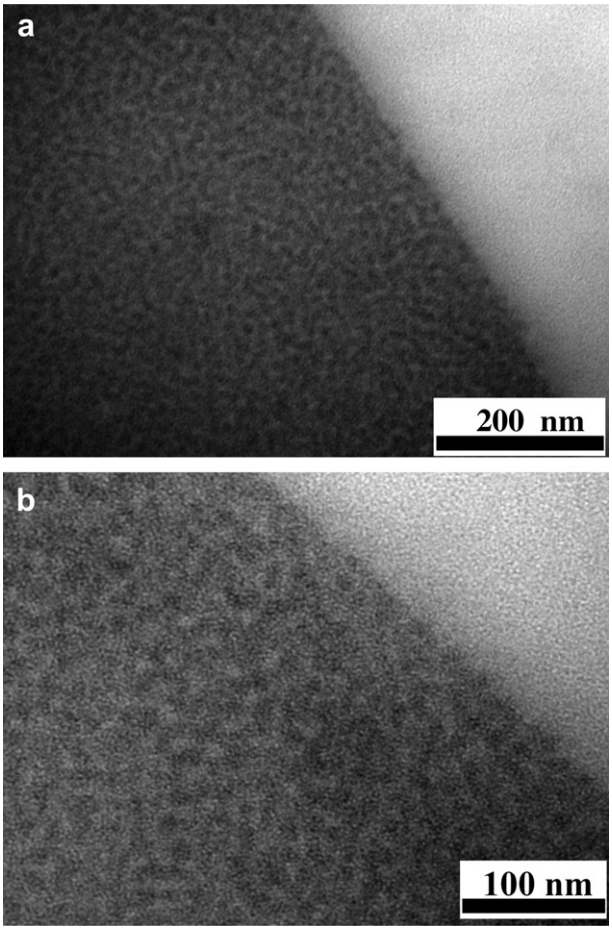

Fig. 2. Cross-sectional TEM micrographs of SEBS electrospun fibers collected at a 1240 m/min take-up velocity at: (a) 25 000 times and (b) 40 000 times for magnification. PS microdomains stained with ruthenium tetroxide were appearing dark.