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Biaxial reinforcements for polybutene-1 medical-tubes achieved via flow-design controlled morphological development of incorporated polystyrene: In-situ microfibrillation, alignment manipulation and performance optimization

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ABSTRACT

By means of goal-directed flow designing and morphology controlling, this paper opened up an efficient method of continuously mass-producing biaxially reinforced polystyrene (PS)/polybutene-1(PB-1) tubes for medical application. The experimental results showed that the PS microfibers were in-situ formed by imposing a specific convergent flow onto the off-die PS/PB-1 blend melt, exhibiting excellent dispersion, high aspect ratio and good interfacial contact. As a result, the ultimate axial strength (UAS) of the microfibrillar PS/PB-1 tubes was enhanced from 29.9 MPa of conventional neat PB-1 tubes to 41.3 MPa. Moreover, by introducing the rotating mandrel or die to modify the flow to helical convergent flow, the formed PS microfiber deviated from axial direction to further improve hoop damage strength (HDS) performances. Particularly, via counter-helical convergent flow extrusion controlled by the counter-rotating mandrel and die system, the opposite-handed helical configuration of PS microfibers was brought out to eliminate the inter-fiber relative slip. As a result, the PS/PB-1 composite tubes exhibited remarkably reinforced mechanical performances in both UAS (40.3PMa) and HDS (34.9 MPa) tests, improved by 34.8% and 48.5% compared to Conv-E neat PB-1. These results suggest that such bi-axially reinforced microfibrillar tubes could be of benefit to ensure the structural integrity of artificial medical tubing systems.

1. Introduction

Polymeric materials have a wide range of desirable attributes that lend themselves to increased use in medical applications. Offering disposability, amenability to gamma and e-beam sterilization, which effectively reduce the occurrence of infection, polyolefin single-use devices, e.g. tubes, pipelines, catheters, are recognized as the most recommended medical products [1,2].

It is vital to note that serious damage and infection could be caused to the patient due to the failure of medical piping systems, especially when they are implanted as catheters, artificial tracheas or drug-infusing tubes [3]. To lower the risk of device-failure caused medical accident, the mechanical resistance of medical tubes can't be overemphasized given the inherently mediocre mechanical properties of many polyolefin-based devices especially under the condition of high strains, loads and elevated temperatures [2–4]. Moreover, the commercialized manufacturing of medical tubes (i.e. melt extrusion) brings about deleterious features to the devices in terms of weld lines and axial orientation, which lead to even flawed end-use mechanical performances of the plumbing devices particularly in the hoop direction [4,5]. When the tubes were under hydrostatic pressure, infusing patients with drugs in intensive care, cracks often generate at the welded joints and propagate along the axial direction leading to the complete failure of the tubes [3,4,6,7].

Studies from academics and industry, by means of introducing fibers (glass, carbon, Kevlar etc.), or nano-sized fillers (carbon nanotubes, graphene etc.) for the purpose of reinforcing polymeric devices, have been extensively carried out for decades [8,9]. Nevertheless, due to the inherent deficiencies of these fillers, namely, poor dispersion, weak interfacial load transfer, random alignment etc., the "reinforcements direct-filling" techniques often fail to live up to expectations [10,11]. In recent years, the emergence of a new

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group of polymer micro- or nano-composites, distinguished by perfect distribution of micro- or nano-fibrillar structure via the concept "converting" instead of "adding", i.e. converting the bulk polymer into micro- or nano-composites instead of adding the fillers into the matrix, have been arousing widespread research interests [5,11–14]. Nevertheless, this technique, via which the microstructure (in this case, microfibers) were gained by the "blending" "drawing" "isotropization" three–step process, is of low-efficiency for continuous tubing extrusion. Moreover, since the in-situ formed microfibers tend to align along the extrusion direction (flow direction) [11–15], this microfibrillation technology still confronts the difficulty of balancing the mechanical properties of the tubes in both axial and hoop directions, especially in current case, the mechanical performance in hoop direction (perpendicular to flow) is of particular importance.

For the purpose of bi-axially reinforcing polybutene-1(PB-1), a semi-crystalline polyolefin which finds potential application in medical-purpose plumbing systems with excellent resistance to chemicals, solvents and creep even at elevated temperatures [16,17], we reported a novel microfibrillar candidate: polystyrene (PS) in combination with a self-designed flow controlled extrusion device. Helical convergent flow was adopted to induce the in-situ formation of helically-aligned PS microfibers and continuously mass-produce PB-1 tubes with superior mechanical properties [18]. In this study, firstly, rheological manifestations of the chosen polymer systems were characterized and analyzed to indicate the morphological evolution mechanism and requirements, to guide the subsequent processing. Then we systematically revealed that by controlling the flow field parameters (convergent flow ratio, hoop velocity, flow pattern), the formation, alignment direction and helical configuration of the microfibers can be simultaneously manipulated to achieve excellent biaxial reinforcement for PB-1 tubes. As a result of the microfibers' excellent dispersion and alignment, good interfacial load transfer and optimized hierarchical configuration, the mechanical performances of the PS/PB-1 composite tubes in both axial and hoop direction were significantly improved as compared to conventional neat PB-1 tubes.

2. Experimental section

2.1. Materials

The raw materials used in this study were polybutene-1(PB-1) and polystyrene (PS). The PS (666H), the microfibrillar candidate, was a general purpose polystyrene supplied in pellets by Styron with a melt flow index (MFI) of 8.0 g/10 min (200 °C/5 kg). The PB-1 matrix was P5250, provided by Mitsui Chemicals Co. Ltd used for tubing extrusion, and its MFI was 0.4 g/10 min (190 °C/2.16 kg).

2.2. Sample preparation

The dried granules of PB-1 and PS in a weight ratio of 90/10, 80/20 and 70/30, were mixed and melt blended in a HAAKE Rheomix OS Lab Mixer at 190 °C for 5 min with rotating speed of 40 rpm. Along with pure PS and PB-1, the blends were compression molded at 190 °C into 1.5 mm thick plates (25 mm in diameter) for rheology tests.

The pre-dried granules of PS and PB-1 in a weight ratio of 10/90 were manually mixed and fed into a self-designed tubing extrusion system as described in supplementary information (SI-Fig. 1). Different off-die flows were designed for the purpose of evolutionarily studying three aspects of current technology:

Inducing the formation of in-situ PS microfibers: By applying vacuum sizing sleeves with various specifications and manipulating the ratio of extrusion/extraction rates, we introduced an extensional convergent flow to the off-die melt with different convergent flow ratio (CFR∅), which was defied as the ratio of melt flow velocity after and before convergence ($\varnothing = \frac{V_2}{V_1}$, where V_2 and V_1 were the melt flow rate in the sizing sleeve and the die respectively). Tubes were prepared at different CFR to determine the optimal condition for inducing the formation of PS microfibers in PB-1 matrix. It's found that when controlling the CFR at 3.4, the microfibers with high aspect ratio formed [18]. The microfibrillar PS/PB-1 produced via this simplex convergent extrusion technique was named as Simp-CE PS/PB-1. For comparison, the conventional extruded neat PB-1 tubes (denoted as Conv-E neat PB-1) were also produced by applying the same CFR to the PB-1 melt, and the common blend of PS/PB-1 (denoted as CB-PS/PB-1) were prepared by plucking the off-die tubular extrudates directly and cooled by water spray.

Manipulating the alignment angle of in-situ formed microfibers: Aiming at manipulating the alignments of in-situ PS microfibers, an off-die relative motion was applied to the convergent-flowing melt by the rotating mandrel to modify the flow pattern from a simplex convergent flow to a helical convergent flow. In order to determine the optimized microfibers' deflection angle for good reinforcements, different mandrel rotation rates were applied to investigate the relationship between the hoop velocity and the deflection angle. In this study, the tubes were fabricated when the mandrel rotation rates were set at 0, 2, 4, 6 rpm, denoted as MR0- (also known as Simp-CE), MR2-, MR4-, MR6-PS/PB-1 respectively. The deflection angle was measured as the angle between microfibers' alignment direction and axial direction.

Control over the hierarchical configuration of helically-aligned microfibers: For the purpose of controlling the hierarchical configuration of in-situ microfibers, a multiple off-die relative motion was applied to the convergent-flowing melt by the simultaneously rotating mandrel and die with rotation rate of 4 rpm. The microfibrillar PS/PB-1 composite tubes fabricated through this co-helical or counter-helical convergent extrusion technique were denoted as CoH-CE PS/PB-1 and CounterH-CE PS/PB-1, respectively.

PS/PB-1 composite tubes were continuously mass-fabricated through methods described above, with 20 mm in outer diameter and ~1.6 mm in thickness (CFR = 3.4). All specimens were aged at room temperature for more than 10 days before any further characterization were conducted.

2.3. Characterizations

Rheology: Rheological measurements were carried out on a 25 mm-parallel-plate rotational rheometer using 1 mm gap. Oscillatory strain sweeps were conducted to ensure all dynamic frequency sweeps were kept within the linear viscoelastic regime. Then dynamic frequency sweeps of pure PS and PB-1 samples were carried out in a frequency range from 100 to 0.01 rad/s using 10% strain (γ) at 190 °C, 200 °C, 210 °C, 220 °C. Following the well-known time–temperature superposition principle, all curves were shifted to reference temperature 190 °C to generate master-curves. The dynamic frequency sweeps (ω = 0.005–100 rad/s) of the blend samples with different PS weight proportion (10%, 20%, 30%) were performed at 190 °C also using 10% strain.

Scanning Electron Microscopy (SEM): The samples were firstly cut off from the produced tubes and etched in a permanganic etchant [19] for 12 h to partly remove the PB-1 matrix before SEM observation was performed. Showing good resistance to permanganic etchant, PS phase was well exposed to construct imaging contrast [20].

2-Dimensional Small/Wide Angle X-ray Scattering (2D-SAXS/WAXD): The specimen were carefully cut from the tubes to obtain