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Investigation of the thermal, mechanical, electrical and morphological properties of supercritical carbon dioxide assisted extrusion of microphase-separated poly(styrene-ethylene/butylene-styrene)

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ABSTRACT

This study investigates the effect of supercritical fluid carbon dioxide ($scCO_2$) assisted extrusion on the thermal, mechanical, electrical, and morphological properties of microphase separated Poly(styrene-ethylene/butylene-styrene) [SEBS] triblock at various critical pressures. Thermal degradation analysis reveals 50 °C enhancement in thermal stability of SEBS when extruded with $scCO_2$ compared to SEBS extruded without $scCO_2$. Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) show improved phase separation due to the breakdown of domain size between the hard and soft block and damping losses represented by tan delta. It was found that SEBS processed with $scCO_2$ has low elastic modulus because of foaming as well as restructuring of hard phase around the soft component. Fourier Transform Infrared Spectroscopy (FTIR) shows the interaction of $scCO_2$ in aromatic phenyl rings of S-rich domain in SEBS. Dielectric spectroscopy analysis also confirms $scCO_2$ results in the difference in relaxation of soft and hard blocks within triblock.

1. Introduction

Supercritical fluid (SCF) is defined as any substance with both pressure and temperature above its critical values. Researchers have reported that SCF offers unique characteristics such as, gas-like diffusivity, liquid-like density, low viscosity and surface tension when compared to conventional organic solvents [1,2]. Among SCF's, it is well known that supercritical carbon dioxide ($scCO_2$) provides good solubility in molten polymers and acts as a plasticizer resulting in a decrease in the viscosity of the molten polymer, the melting point, and the glass transition temperature [2–4]. These changes in turn result in fractionation of polymer, modifying the mechanical, as well as physical properties of the polymer [3–7].

The uses of thermoplastic elastomers (TPEs) for research and commercial applications are rapidly growing due to its diversity and versatile potential for electro-responsive and nanocomposite applications [8]. TPEs possess unique properties because of their physical mixing of hard thermoplastic and soft rubber elastomer resulting in easy processability and recyclability [9]. Poly(styrene-ethylene/butylene-styrene) [SEBS], a type of styrene based TPE, is a hydrogenated elastomer consisting of polystyrene (hard S block) at both ends and poly(ethylene/butylene) (the soft EB block) in the middle. This intervening and interfacial structure of TPE SEBS provides a perfect combination of mechanical strength, flexibility, and temperature resistance [10–12]. Many research groups have reported that block copolymers possess a well-ordered phase separated microstructure depending on the composition of individual block polymer. However, continuous microstructure transitions are observed with temperature increments affecting the mechanical strength, rheology, and morphology [10–14].

Rauwendaal [15] defined melt extrusion as the process of transforming raw materials into an artefact of uniform shape and density under controlled conditions by forcing the material through a restricted orifice called a die [15–17]. Therefore, it is highly likely that the combination of extrusion process and $scCO_2$ would benefit processing of polymers with lower processing temperatures and/or act as a foaming agent during expansion through the die [3,4,7]. Moreover, the supercritical conditions for CO_2 are easily achieved (T_c = 304.15 K, P_c = 7.38 MPa) and can be removed from the system by simple

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depressurization [4,6,18–22]. It is a general representation that CO_2 solubility in a polymer is a function of pressure and temperature [3,4,23], yet, specific molecular interaction between CO_2 and polymer holds has considerable impact in terms of solubility and diffusivity.

Sameer et al. [6], Kazarian [1] and other researchers have reported that CO_2 has the potential to act as both a weak Lewis acid and Lewis base due to its quadrupole moment, indicating that CO_2 may solubilise dipolar and non-dipolar molecular structures through site-specific solute–solvent interactions [23–25]. However, the solubility and diffusivity of CO_2 in polymers are not only subjective to the interaction between molecular chains but also on the crystalline or amorphous nature relating to the free volume of the polymers [6,23,24]. In the case of SEBS, weak Lewis acid-base interaction with CO_2 is initiated due to the phenyl ring in PS, resulting in sorption and swelling of SEBS [3,4,6,24]. Although numerous studies exist in scientific and industrial communities using SCF batch processing technique, a dearth of knowledge still persists on the use of SCF for continuous industrial standard polymer manufacturing process such as hot melt extrusion. In addition, the scientific understanding on how SCF affects the thermal, mechanical, electrical, and morphological properties of phase separated thermoplastic elastomers (TPEs) using hot melt extrusion remains unexplored. Therefore, complete use of $scCO_2$ assisted extrusion of TPEs is limited for commercial applications. This study investigates the effects of $scCO_2$ assisted extrusion on thermal, mechanical, electrical, and morphological properties of microphase separated styrene based TPE.

The effect and benefits of supercritical assisted extrusion on the structure property behaviour of SEBS are presented. The impact of $scCO_2$ assisted extrusion of SEBS at different critical pressures was investigated for the first time using Thermogravimetric Analysis (TGA), modulated differential scanning calorimetry (MDSC), dynamic mechanical temperature analysis (DMA), tensile test, Fourier transform infrared spectroscopy and morphology analysis. The main aim of the paper is show the promising possibilities of $scCO_2$ assisted extrusion technology for improved microphase separation of TPEs for their superior performance in a wide range of applications. This work possesses high impact for the formation of highly phase separated domains for actuation, dielectric energy harvesters, flexible capacitors and other electomechanical applications.

2. Materials and experimental methods

2.1. Materials

SEBS (Kraton® G1652E Polymer) with linear triblock structure and styrene/rubber ratio of 29/71 was supplied by Kraton polymer research, Belgium. The received SEBS was stored at room temperature for several months before extrusion and material characterization.

2.2. Extrusion of SEBS

SEBS was extruded in a co-rotating twin-screw extruder with L/D ratio of 40:1. Extrusion was carried out at a screw speed of 55 revs/min, and temperature profile of 150–240 °C, over nine zones. An additional setup consisting of injection pump, chiller and CO_2 cylinder was used for continuous feeding of supercritical fluid CO_2 at constant flow rate of 2 ml/min at various pressure of 800 psi, 1000 psi, and 1200 psi during the extrusion of SEBS. The extrudate was then passed through a chilling roller system at 20 °C running at a constant speed of 0.9 m per minute to produce constant thickness sheet of 1 mm.

2.3. Thermogravimetric analysis

The degradation and thermal stability of all extrudates were performed using TGA Q50, TA instruments. TGA measures weight changes in a material as a function of temperature under a controlled atmosphere. All the samples were run from 20 °C to 550 °C at the heating rate of 10 °C/min.

2.4. Modulated differential scanning calorimetry

All MDSC experiments were carried out using TA Instruments TA2000. About 10 mg of sample was encapsulated and hermitically sealed in aluminium pans. The sample and reference pans were matched for accurate heat capacity measurements. The heat capacity was calibrated using sapphire, while temperature and baseline were calibrated using indium. An oscillation period of 60 s and amplitude of ± 0.47 °C were used in modulated heating and cooling experiments. SEBS was subjected to rapid cooling to −80 °C followed by heating at 3 °C/min to 240 °C. At the beginning and end of each heating and cooling cycle, SEBS was held isothermally for 3 min. TA software for MDSC was used for recording, analysis and deconvolution of the signals. Least square method was used to smooth all the curves for better analysis. The level of smoothing was selected within the range of 8–12 to give minimum distortion and no shift of peaks. In all MDSC figures, the exotherm points upwards. All the results are performed as n = 3 replicates with standard deviation less than 2%.

2.5. Dynamic mechanical thermal analysis

Tensile flat samples were prepared by cutting an extruded sheet along the axis of screw rotation obtained from co-rotating, twin screw extrusion. Dynamic mechanical analysis was carried out on a TA Instruments DMA 800 to evaluate the structural properties of SEBS. The experiment was carried out in a ramp temp/multi frequency mode at an amplitude of 16 μm from 25 to 120 °C at a frequency of 1 Hz with a heating rate of 3 °C/min. Results are presented as average values of n = 3 replicate experiments with standard deviation.

2.6. Mechanical testing

Tensile testing of supercritical assisted extrusion of SEBS was performed using Zwick/Roell Z010 with 2.5 kN load cell with a crosshead speed of 500 mm/min and maximum extension of 500%. The extrudates were cut per ASTM 638 Type I dumbbell shape specimen along the axis of twin screw rotation. Results are presented as average values of n = 5 replicate experiments with standard deviation.

2.7. Attenuated total reflectance − Fourier transform infrared spectroscopy (ATR- FTIR)

Phase separation due to SEBS − $scCO_2$ interaction was studied using ATR-FTIR. Infrared spectra of all composites were obtained with a VARIAN 600 ATR-FTIR. ATR-FTIR spectroscopy analysis was carried out at room temperature on clean solid extruded flat samples with a resolution of 4 cm^{-1}. All data were collected between 600 cm^{-1} and 4000 cm^{-1} with an average of 32 scans.

2.8. Dielectric analysis

A Solatron 1260 impedance analyser with a 1296 dielectric interface was used for the dielectric characterisation of all flat samples. The material was placed in between two circular electrodes of 10 mm diameter and a 3Vrms alternating voltage was applied. Thickness for all samples were between 1 and 2 mm

2.9. Morphology analysis

Surface characterization was done using Hitachi S-3000N Variable pressure electron microscope at accelerating voltage of 20 kV and resolution 500 μm to observe the porosity of SEBS under different pressure condition. Typical micrographs of extrudates along the axis direction of extrusion were taken.