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Blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with polystyrene-based thermoplastic rubbers: A comparative study

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Abstract

This work presents the first part of our study on the modification of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with styrenic thermoplastic rubbers. Polystyrene-*b*-polyisobutylene-*b*-polystyrene (SIBS), polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene (SEBS) triblock copolymers were melt blended with PPO and the blends were characterized. Differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and transmission electron microscopic (TEM) studies revealed that PPO/SEBS blends displayed the most pronounced phase-separated morphology with largest rubbery domains. SBS showed the most miscibility, and the least detrimental effect on dynamic mechanical properties and tensile strength. The results of this comparative study guided us to develop optimum conditions for the impact modification of PPO by SIBS thermoplastic rubbers.

Keywords: Polymer blend; Poly(2,6-dimethyl-1,4-phenylene oxide); Styrenic thermoplastic rubbers (SIBS, SEBS, SBS)

1. Introduction

PPO (or PPE) (Poly(2,6-dimethyl-1,4-phenylene oxide or ether)) is a very attractive material due to its high strength, high heat distortion temperature, chemical resistance, stiffness, and fracture toughness [1,2]. However, its brittleness and poor processability have limited its industrial use in a wider range of applications [2]. In order to achieve desired mechanical properties PPO has been blended with various materials [2–10]. Since PPO and polystyrene (PSt) are completely miscible at all molecular weights and concentration ranges [3,4], PSt or its derivatives, such as high-impact PSt (HIPS, or polybutadiene-grafted polystyrene resin) and PSt-based block copolymers, have been used to improve the processability and toughness of pure PPO [5]. A good example is Noryl® by General Electric, an important engineering plastic produced by blending PPO with HIPS. Styrenic thermoplastic rubbers, such as polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and its hydrogenated version, polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene) (SEBS), and polystyrene-*b*-polyisobutylene-*b*-polystyrene (SIBS) have also been blended with PPO [2–4,6–10]. This latter is a relatively new type of thermoplastic rubber, which has become available commercially [11]. SIBS is chemically similar to SEBS in a sense that it has saturated elastomeric midblocks, and it demonstrates excellent chemical, oxidative and environmental stability [12]. Fig. 1 compares the chemical structures of the various thermoplastic rubbers. These materials exhibit thermoplastic elastomeric behavior, combining the good processability of thermoplastics with rubber elasticity. Ideally, the elastomer phase of the block copolymer should possess a solubility parameter sufficiently different from that of the PPO matrix to ensure fine phase dispersion, but the plastic phase should be compatible with PPO to ensure adequate adhesion of the elastomer phase to the matrix

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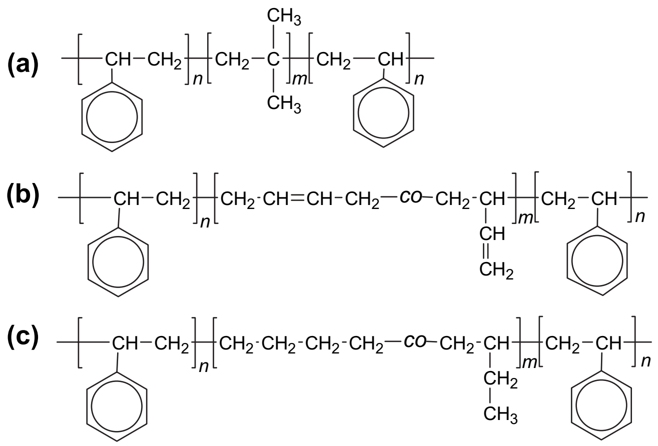

Fig. 1. Chemical structure of various thermoplastic elastomers: (a) SIBS, (b) SBS and (c) SEBS.

[13]. It has been shown that even though PPO is completely miscible with PSt, the elastomeric blocks in the thermoplastic rubber may prevent free dispersion of the PSt blocks within the PPO matrix. Tucker et al. reported that PPO is completely miscible with SBS, while immiscible with SEBS having relatively short PSt arms ($M_n < 14{,}000$ g/mol) [3,6]. The authors found no effect of the molecular weight of PPO on miscibility in the $M_n \sim 15{,}000$–$30{,}000$ g/mol range. Chiu and Hwung reported that the miscibility of the blends decreased with increasing elastomer segment's molecular weight [7]. Asthana and Kennedy demonstrated that PPO/star-branched SIBS prepared by solution blending [10] had good miscibility when low MW PPO ($M_n = 3100$ g/mol) was used, but were only partially miscible with higher MW PPO ($M_n = 10{,}500$ g/mol).

Given the interest in using thermoplastic rubbers for toughening of PPO, this work reports our first results concerning the thermal, mechanical and morphological properties of PPO/SIBS blends prepared by melt compounding, in comparison with PPO/SBS and PPO/SEBS blends.

2. Experimental

2.1. Materials

PPO ($M_n = 24{,}000$ g/mol, $M_w/M_n = 1.5$) without any PSt addition was provided by BASF AG. SIBS triblock copolymers (SIBS 103T, $M_n = 78{,}310$ g/mol, MWD = 1.74, 34 wt% PSt, and SIBS 073T, $M_n = 66{,}720$ g/mol, $M_w/M_n = 1.24$, 31 wt% PSt) were provided by Kaneka Co, Japan. Shell kindly provided SEBS (Kraton G1650, $M_n = 80{,}890$ g/mol, MWD = 1.01, 29 wt% PSt) and SBS (Kraton D1153, $M_n = 86{,}000$ g/mol, MWD = 1.01, 30 wt% PSt).

The molecular weight (MW) and molecular weight distribution (MWD) of the block copolymers were determined by SEC using a Waters system equipped with six Styragel-HR columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å pore sizes), thermostated at 35 °C, a Waters 410 DRI detector thermostated at 40 °C, a Dawn DSP 18 angle Laser Light Scattering (MALLS) detector (Wyatt Technology), and a Waters 996 UV detector. THF was used as a mobile phase at 1 ml/min, continuously distilled from CaH_2 and recirculated. The Astra software (version 4.73) controlled the acquisition of data from the detectors and processed the data to obtain MWs. The MW of SBS and SEBS was measured by using the 100% mass recovery method; the MW of SIBSs was measured by both known d*n*/d*c* (copolymer d*n*/d*c* was calculated based on the weight fraction and d*n*/d*c* of the individual components, PIB = 0.093, PSt = 0.183) and 100% mass recovery on the SEC columns. The PSt content of the SIBS blocks was measured by ^{1}H NMR using a Varian Gemini 400 MHz and deuterated-chloroform (*d*-$CDCl_3$) solvent. Material properties are summarized in Table 1; the values agree well with the nominal values provided by the manufacturers.

2.2. Blend and test specimen preparation

PPO/block copolymer blends with compositions of 95/5, 90/10, 80/20 (w/w) were prepared using a Brabender Plasticorder mixer (DSE 20/40) at a rotor-speed of 50 rpm. The temperature of the mixer was 240 °C, well above the glass transition temperature (T_g) of PPO (216.6 °C). Nitrogen gas was introduced during mixing to minimize oxidative degradation of the PPO or block copolymers. PPO was first added to the mixer slowly and was allowed to soften. Shortly thereafter, the block copolymer was added and mixed for 4 min. All blends were pulverized into small particles (the diameter of particles was less than 0.5 mm) and dried at 100 °C for more than 2 h before compression molding. The blends were compression molded into sheets at 280 °C for 20 min in an electrically heated hydraulic press at a pressure of 40 kN (10 min preheating without pressure, and then 10 min with 40 kN pressure). After compression molding, the plates were transferred to a water-cooled press where they were held at 80 kN for 30 min.

2.3. Differential scanning calorimetry (DSC)

Samples of 5–10 mg were placed into aluminum sample pans and sealed for testing in a METTLER TOLEDO DSC821. The heating rate was 20 °C/min, and the data were collected from the second and third scans. Glass transition temperatures (T_gs) were taken as the mean value between the onset and end point temperatures. Nitrogen atmosphere was used to minimize thermal degradation of the blends.

Table 1
Characterization of thermoplastic rubbers

Sample ID	M_n (g/mol)	M_w/M_n	PSt (wt%)	M_n PSt block (g/mol)	M_n elastomer (g/mol)	M_c (g/mol)
SIBS103T	78,300	1.74	34.2	13,400	51,500	9610
SIBS073T	66,700	1.24	31.0	10,300	46,100	9610
SEBS	80,900	1.01	29.0	11,600	57,700	1530
SBS	86,500	1.01	30.0	12,900	60,700	2150