

Near-surface morphology effect on tack behavior of poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer/rosin films

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Abstract

The correlation between near-surface morphology and tack behavior of poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (SBS)/rosin ester films was investigated using probe tack tests, transmission electron microscopy and small-angle X-ray scattering. The SBS/rosin films with rosin composition between 10 and 20 wt% rosin, prepared by slow evaporation of toluene during solvent casting, exhibited uniform near-surface morphology of lamellae oriented parallel to the surface. However, due to the limited solubility of rosin in the PS domains, the rosin started to phase-separate from the PS domains at 15 wt%, and formed fully separated micron-sized domains above 20 wt% rosin. The probe tack force of the SBS/rosin films increased steadily when the near-surface domain orientation changed from perpendicular cylinder to parallel lamellae on addition of rosin. Specifically, for a given lamellar morphology and surface orientation, macrophase separation of rosin plays a critical role in determining the tack properties of SBS/rosin films.

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1. Introduction

The tack properties of materials are important factors in determining the potential of these materials as pressure sensitive adhesives and hot melt adhesives. Elastomer-based adhesives using blends of poly(styrene-*b*-butadiene-*b*-styrene) (SBS), poly(styrene-*b*-isoprene-*b*-styrene) (SIS), or poly(styrene-*b*-ethylene-butylene-*b*-styrene) (SEBS) triblock copolymers with tackifiers have been widely studied as pressure sensitive adhesive materials [1–7]. Tack is defined as an adhesive's ability to form a physical bond with a heterogeneous surface in a shorter contact time and at a lighter pressure than required for adhesion tests [8]. Since, (shear) adhesion tests typically employ low strain rates and intermediate stress levels during contact, adhesion properties commonly reflect a large-scale deformation such as flow or plastic deformation under contact stress, over a long period of time. On the contrary, due to the relatively shorter contact times for tack tests compared to adhesion tests,

pseudo-elastic deformations without macroscopic flow near the surface should play an important role in determining the tack properties [9]. In order to obtain the required tack property, adhesives must have relatively low moduli and short relaxation times to relieve internal stresses [2,10]. In such cases, low molecular weight resins are added as tackifiers to increase the flow properties and surface wettability, based on its compatibility with either the softer or harder block domains of the thermoplastic elastomer. Softer block-associating resins decrease the rubbery plateau modulus, resulting in improved tack, whereas the harder block-associating resins decrease the cohesive strength of the matrix [11].

Many studies on elastomer/tackifier blends have concentrated on balancing the ability to 'hold onto the adherend' and to 'be cleanly removed from the adherend' [1–11]. Aubrey et al. suggested that the surface energy and deformability of adhesives play an important role in the bonding and debonding process during tack tests [12]. According to Galan et al., the formation of the macrophase-separated resin domains and the tack strength of the adhesive are significantly changed by the presence of the microphase structure when either the mid or end block domains are saturated by the tackifier resins [1]. Considering the near-surface morphology of the block copolymer, the chain connectivity in block copolymers imposes limitations on

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the degrees of freedom of molecules near the polymer-air interface [13–18], and it is generally known that block chains with lower surface energy cover the free surface even when the component having higher surface energy forms the matrix [17,18]. Kim et al. found that perpendicularly oriented PS cylinders with higher surface energy exist beneath the PB layer in thermally annealed SBS thin films [16]. Hasegawa and Hashimoto observed similar behavior for SI and SB diblock copolymer blends, i.e. they found that the component with the lowest surface energy covered the free surface [17].

Our report investigates the role of near-surface morphology on tack behavior of an elastomer-based adhesive with a tackifier resin. This work shows the correlation between the tack behavior of elastomer-based adhesives and the near-surface morphologies, in particular, the micro-domain orientation and the macroscopic phase separation of the tackifier resin. An SBS triblock copolymer is used as the elastomer, and a rosin ester is used as the tackifier resin, which is selectively more miscible with PS than with PB.

2. Experimental

The SBS triblock copolymer (Kraton D1101, Shell Company) with 14 wt% SB diblock copolymer was used as a base elastomer. The molecular weight (M_w), polydispersity (PDI), and the styrene content were 136,000 g/mol, 1.15, and 33 wt% PS, respectively, [19]. The tackifier used was a commercial rosin ester (KO-90, Kolon Chemical Co., Korea), which contains a mixture of different ester branch numbers (an average of 3.8 branches, given that its average M_w is 1200 g/mol). The glass transition temperatures (T_g) of the rosin ester (50 °C), PS (98 °C) and the PB (−86 °C) domains in SBS were determined using differential scanning calorimetry (DSC).

SBS/rosin blends with rosin contents ranging from 0 to 30 wt% were prepared by solvent-casting a 5 wt% toluene solution of SBS/rosin onto 70 μm thick polyester film substrates. Then, the solvent was slowly evaporated at room temperature over a period of 7 days. Finally, the SBS/rosin films were annealed under vacuum at 120 °C for 4 days. The thickness of the resulting films was controlled to achieve 2 mm and 200 μm for rheology and probe tack tests, respectively.

The dynamic temperature sweep experiments for the SBS/rosin blends were performed in the temperature range of −120–120 °C on a Rheometrics Dynamic Spectrometer (RDS-II, Rheometrics) using parallel plates (16 mm diameter plates with a 2 mm gap), at a heating rate of 2 °C/min, an angular frequency (ω) of 1 rad/s and a strain amplitude (γ_0) of 0.5, which lies in the linear viscoelastic region.

The change in morphology of the SBS/rosin blends containing different rosin contents was observed using a transmission electron microscope (TEM) (1200EX, JEOL), operating at an accelerating voltage of 120 kV. The bulk and near-surface regions of the SBS/rosin blends were cut to approximately 50 nm thick using a cryogenic ultramicrotoming system (MT-7000, RMC). The films were first embedded using an epoxy kit (Poly/bed 812, Polysciences Inc.) for easy handling, and stained with 2 wt% osmium tetroxide (OsO_4)

solution for 12 h. The stained samples were then cut using a diamond knife at −120 °C.

Small-angle X-ray scattering (SAXS) experiments for the solvent-cast and annealed SBS and SBS/rosin blends (2 mm thickness) were performed at the 4C1 beam line in Pohang Accelerator Laboratory (PAL), Korea. The wavelength λ of the incident X-ray beam was 0.1608 nm, and the distance between the sample and the 2D detector (SCX-TE/CCD-1242E, Princeton Instruments Inc.) was 180 cm. The q ($=4\pi \sin \theta/\lambda$) range was calibrated using a standard SEBS sample of well-defined structure. All SAXS profiles were normalized to the primary X-ray intensity using the signal of ionization chambers placed on either side of the sample. The 2D SAXS profiles were then converted into 1D profiles through circular averaging.

The probe tack tests on 200 μm solvent-cast SBS or SBS/rosin films were performed using a commercial probe tack tester (Texture Analyzer, Stable Micro System Ltd) in adhesion mode fitted with a 5 mm stainless steel probe. The probe contact force and time were 100 g and 10 s, respectively.

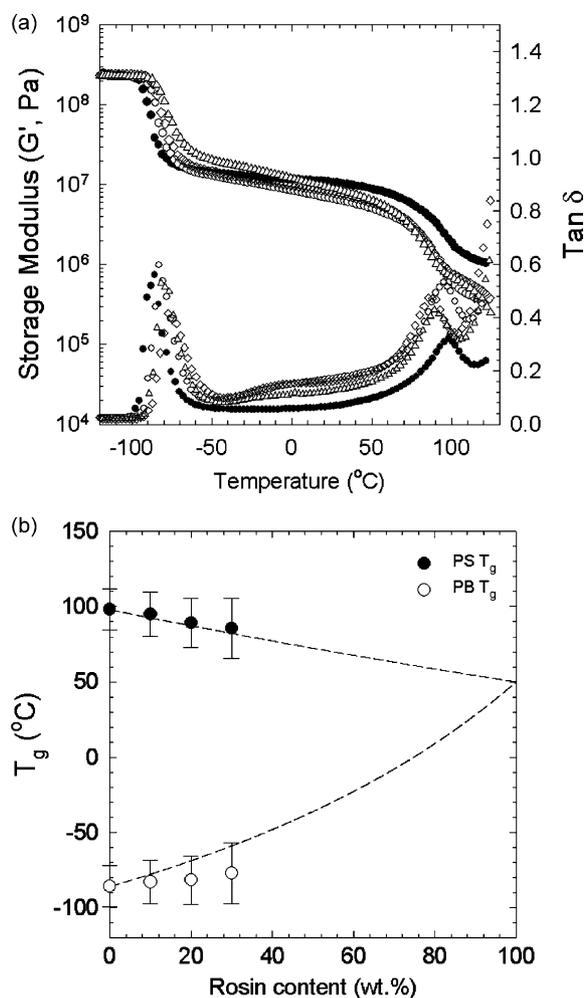


Fig. 1. (a) Storage moduli (G') and $\tan \delta$ of SBS/rosin blends containing increasing rosin contents as a function of temperature (●, SBS; ○, 10 wt%; ▲, 20 wt%; ◇, 30 wt% rosin). (b) T_g values of PS and PB domains in SBS/rosin blends as a function of the rosin content. (The broken lines represent the T_g predictions by the Fox equation [20]. The error bar represents the full-width half maximum of $\tan \delta$).

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