Matrix-Free Polymer Nanocomposite Thermoplastic Elastomers

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Supporting Information

ABSTRACT: Thermoplastic elastomer (TPE) grafted nanoparticles were prepared by grafting block copolymer poly-(styrene-block-(n-butyl acrylate)) onto silica nanoparticles (NPs) via surface-initiated reversible addition–fragmentation chain transfer (RAFT) polymerization. The effects of polymer chain length and graft density on the mechanical properties were investigated using films made solely from the grafted NPs. The ultimate tensile stress and elastic modulus increased with increasing PS chain length. The dispersion of the silica NPs and the microphase separation of the block copolymer in the matrix-free polymer nanocomposite were investigated using small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The higher polymer graft density TPEs exhibited better microphase separation of the block copolymers and more uniform silica NP dispersion than lower polymer graft density TPEs with similar polymer chain length and composition.

INTRODUCTION

Thermoplastic elastomers (TPEs) have broad applications in a variety of fields as footwear, paving, replacement of vulcanized rubber, adhesives, sealants, coatings, automotive, medical, etc.1,2 The traditional and widely used TPEs are made from triblock copolymers such as poly(styrene-block-isoprene-block-styrene) (SIS), which are synthesized by living anionic polymerization.3,4 Traditional ABA type TPEs contain a glassy domain dispersed within a rubbery domain formed from microphase separation of the block copolymer. Recent developments in controlled radical polymerization techniques have added additional tools for the design and synthesis of new architectures of polymer materials.5–8 Jerome et al. reported TPEs formed from poly(methyl methacrylate-block-(n-butyl acrylate)-block-methyl methacrylate) (PMMA-b-PBA-b-PMMA) by atom transfer radical polymerization (ATRP).9 They also compared the differences in morphology and mechanical properties with an identical block copolymer prepared by anionic polymerization. Luo et al. prepared a series of thermoplastic elastomers of poly(styrene-block-(n-butyl acrylate)-block-styrene) (PS-b-PBA-b-PS) by reversible addition–fragmentation chain transfer (RAFT) emulsion polymerization.10 In addition to the traditional TPEs prepared by ABA triblock copolymers, new architectures of thermoplastic elastomers have been reported, such as star block copolymers,11–15 comb multigrafted copolymers,14–16 etc. Matyjaszewski et al. reported a thermoplastic elastomer formed by 10- and 20-arm star-like block copolymers, poly(ε-caprolactone-block-methyl methacrylate) (PBA-b-PMMA), from short linear multifunctional initiators.17 The ultimate tensile strength and the elastic modulus increased as the number of arms increased. Tang et al. prepared a thermoplastic elastomer by random copolymer-grafted cellulose with the rigid cellulose backbone dispersed in soft matrix random copolymer PBA-co-PMMA (0.9–3.4 wt % cellulose).18 Inorganic nanoparticles can be added to polymer matrices as nanofillers to tune the mechanical properties.19,20 The dispersion of nanoparticles in the matrix was crucially important to the mechanical properties of polymer nanocomposites.21–26 Polymer grafted nanoparticles can self-assemble into well-defined structures27–30 and increase the compatibility of nanoparticles with the polymer matrix.25,26,31,32 The dispersion of the nanoparticles in polymer nanocomposites was mainly dependent on polymer graft density and the ratio of molecular weights of grafted polymer and matrix polymer.13–16 Mondragon et al. reported the use of polystyrene grafted magnetic nanoparticles to improve the dispersion of magnetic nanoparticles in a SBS thermoplastic elastomer matrix.34 Polymer nanocomposites formed by one-component polymer grafted NPs, which were also referred to as matrix-free nanocomposites, had advantages over the traditional nanoparticle filled matrix systems. The matrix-free nanocomposite overcame the demixing issue because the polymers were chemically tethered to the NPs.38 However, there are very few reports of thermoplastic elastomers formed by matrix-free organic/inorganic polymer nanocomposites. Recently, Wang et al. reported thermoplastic elastomer composites formed by PBA-co-PMMA grafted multiwalled carbon nanotubes39,40 and Fe3O4 nanoparticles41 prepared using ATRP. The magnetic polymer nanocomposite exhibited higher tensile strength and elastic recovery than the counterpart linear copolymers. To the best of our knowledge, there are no reports of polymer
architecture effects (including polymer grafting density and chain length) on the microphase separation and mechanical properties of films formed by block copolymer grafted inorganic nanoparticles.

Herein we report on thermoplastic elastomers formed by block copolymer grafted silica NPs without additional polymer matrix. The block copolymer, poly(styrene-block-(n-butyl acrylate)) (PS-b-PBA), tethered to 15 nm silica nanoparticles was prepared by RAFT polymerization using a grafting-from strategy. In addition to the PS glassy domains dispersed in the rubbery PBA matrix, the silica nanoparticles also acted as cross-linking sites in the thermoplastic elastomers formed by PS-b-PBA grafted silica nanoparticles (PS-b-PBA-g-SiO$_2$). Three main parameters were used to tune the mechanical properties of the polymer nanocomposite film: chain length of PBA, chain length of PS, and graft density of the polymer chains. We investigated the impacts of these parameters on the mechanical properties of TPEs formed by PS-b-PBA-g-SiO$_2$ (Figure 1).

![Figure 1](image)

**Figure 1.** Comparison of block copolymer PS-b-PBA grafted silica nanoparticles with different chain lengths of PS (A vs B), chain lengths of PBA (A vs C), and chain grafted densities (A vs D).

### EXPERIMENTAL SECTION

**Materials.** All chemicals were purchased from Sigma-Aldrich or Fisher unless otherwise specified. Styrene (>99%) and n-butyl acrylate (>99%) were purified by passing each through a column of activated basic alumina column to remove the inhibitor. 4-Cyano-4-(((dodecylthio)carbonylthio)pentanoic acid (CDPA, >97%) was purchased from Boron Molecular. Colloidal silica particles (~15 nm diameter, 30 wt % in MEK) were supplied by Nissan Chemical. 3-Aminopropyl dimethyloxysilane was purchased from Gelest Inc. 2-Mercaptothiazoline (98%) was purchased from Alfa Aesar. Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol twice before use.

**Characterization.** *Polymer Characterization.* $^1$H NMR (Bruker Avance III-HD 300 and 400 MHz) were conducted using CDCl$_3$ as solvent. Molecular weights ($M_n$) and dispersities ($D$) were determined using a gel permeation chromatograph (GPC) equipped with a Varian 290-LC pump, a Varian 390-LC refractive index detector, and three Styragel columns (HR1, HR3, and HR4, molecular weight ranges of 100–5000, 500–30 000, and 5000–500 000, respectively). THF was used as eluent for GPC at 30°C and a flow rate of 1.0 mL/min. GPC was calibrated with polystyrene (PS) standards obtained from Polymer Laboratories. UV–vis absorption spectra were recorded on a Shimadzu UV-2450. Thermogravimetric analysis (TGA) measurements were carried out on a TA Q5000 thermogravimetric analyzer (TA Instruments). All the samples were preheated to 150°C and kept at this temperature for 10 min to remove residual solvents. After cooling to 40°C, the samples were heated to 800°C with a heating rate of 10°C/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was conducted using a TA Q2000 DSC (TA Instruments) under a nitrogen atmosphere at a heating rate of 10°C/min from 80 to 180°C. Tensile testing was conducted using an Instron 5500 tensile tester with a 100 N load cell with a crosshead speed of 20 mm/min. The dog-bone-shaped samples for tensile testing were cut from hot pressed samples with 22 mm length and 5 mm width. Each sample was tested at least three times for tensile testing. Dynamic mechanical analysis (DMA) was conducted using a RSA3 DMA (TA Instruments) in tensile mode. The DMA data were collected by testing with a frequency of 1.0 Hz, 0.1% strain, and a heating rate of 3°C/min from −100 to 150°C.

**Film Preparation.** Polymer grafted silica nanocomposites were hot pressed on a Carver hotpress at 150°C and 1500 psi for 5 min and then 3000 psi for 30 min to get films with ca. 0.3 mm thickness.

**X-ray Measurement.** Small-angle X-ray scattering (SAXS) experiments were conducted using a SAXSLab Ganesha at the South Carolina SAXS Collaborative. A Xencos GeniX3D microfocus source was used with a Cu target to generate a monochromatic beam with a 0.154 nm wavelength. The instrument was calibrated using National Institute of Standard and Technology (NIST) reference material 640c silicon powder with the peak position at total scattering angle of 2θ of 28.44°. A Pilatus 300 K detector (Dectris) was used to collect the two-dimensional (2D) scattering pattern. The 2D images were azimuthally integrated to yield the scattering vector and intensity. All SAXS experiments were conducted for 1 h with an X-ray flux of 4.1 M photons/s incident up on the sample with a sample-to-detector distance of 1052 mm.

**Electron Microscopy.** Transmission electron microscopy (TEM) was performed on a Hitachi H8000 TEM at an accelerating voltage of 200 kV. The microsectioned sample for TEM was prepared by embedding the film in epoxy resin followed by ultramicrotomy with diamond knife at room temperature to a thickness of ca. 100 nm and transferred to a copper TEM grid.

Surface-initiated RAFT polymerization was used to synthesize PS-b-PBA grafted silica nanoparticles (Scheme 1). Briefly, the silica nanoparticles were reacted with 3-aminopropyl dimethyloxysilane to obtain a primary amine functionalized surface, which was further reacted with activated CDPA RAFT agent. The block copolymer grafted silica nanoparticles were synthesized by sequential polymerization effects (including polymer grafting density and chain length) on the microphase separation and mechanical properties of films formed by block copolymer grafted inorganic nanoparticles.

Herein we report on thermoplastic elastomers formed by block copolymer grafted silica NPs without additional polymer matrix. The block copolymer, poly(styrene-block-(n-butyl acrylate)) (PS-b-PBA), tethered to 15 nm silica nanoparticles was prepared by RAFT polymerization using a grafting-from strategy. In addition to the PS glassy domains dispersed in the rubbery PBA matrix, the silica nanoparticles also acted as cross-linking sites in the thermoplastic elastomers formed by PS-b-PBA grafted silica nanoparticles (PS-b-PBA-g-SiO$_2$). Three main parameters were used to tune the mechanical properties of the polymer nanocomposite film: chain length of PBA, chain length of PS, and graft density of the polymer chains. We investigated the impacts of these parameters on the mechanical properties of TPEs formed by PS-b-PBA-g-SiO$_2$ (Figure 1).

![Scheme 1](image)

**Scheme 1.** Synthesis of PS-b-PBA Grafted Silica Nanoparticles

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ization of n-butyl acrylate and styrene on the surface of silica nanoparticles.

**Activation of RAFT Agent CDPA.** CDPA (4.07 g, 0.01 mol), 2-mercaptotetrazoline (1.31 g, 0.011 mol), and 4-(dimethylamino)-pyridine (DMAP) (0.122 g, 0.001 mol) were dissolved in 100 mL of dichloromethane. The solution was cooled in ice bath, and N,N-dicyclohexylcarbodiimide (DCC) (2.48 g, 0.012 mol) was added slowly to the solution. The solution was warmed to room temperature and stirred for 1 h. After the precipitate was filtered, the solution was concentrated and purified by silica gel column chromatography (hexane:ethyl acetate = 3:1) to get activated CDPA (4.32 g, 86%) as a yellow solid (mp = 58 °C). 1H NMR (300 MHz, CDCl3): δ (ppm) 4.60 (t, 2H, J = 7.5 Hz), 3.68–3.49 (m, 2H), 3.34 (t, 4H, J = 7.5 Hz), 2.68–2.44 (m, 2H), 1.90 (s, 3H), 1.71 (quint, 2H, J = 7.5 Hz), 1.43–1.27 (m, 18H), 0.89 (t, 3H, J = 6.6 Hz). 13C NMR (75 MHz, CDCl3): δ (ppm) 271.1, 201.7, 172.4, 119.2, 56.0, 46.3, 37.1, 34.4, 33.9, 31.9, 29.64, 29.57, 29.44, 29.36, 29.21, 29.0, 28.5, 27.7, 24.9, 22.7, 14.2. HRMS (EI) (m/z) calcd for C20H17N2OS2: 304.1439; found: 304.1431.

**Synthesis of CDPA Anchored Silica Nanoparticles.** Colloid silica nanoparticles (50 g, 30% in MEK), 3-aminopropyldimethyl-ethoxysilane (360 mL) and 50 mL of THF were added to 250 mL round-bottom flask. After purging with N2 for 30 min, the solution was heated to 75 °C overnight and then cooled to room temperature. The solution was poured into 400 mL of hexanes, and amino-functionalized silica nanoparticles were recovered by centrifugation at 3000 rpm for 10 min. The amino-functionalized silica nanoparticles were dispersed in 50 mL of THF and added to the activated CDPA (0.5 g) THF solution slowly. After stirring overnight, the solution was poured into 200 mL of hexanes, and the CDPA-functionalized silica nanoparticles were recovered by centrifugation. The dispersion—precipitation process was repeated until the supernatant was colorless after centrifugation. Finally, the CDPA anchored silica nanoparticles (CDPA-SiO2) were dried in a vacuum oven for 24 h. The graft density of CDPA on silica nanoparticle was analyzed by UV−vis spectra as S5.7 μmol/g (0.24 ch/nm²).

**Synthesis of Poly(n-butyl acrylate) (PBA) Grafted Silica Nanoparticles (PBA-g-SiO2).** CDPA-SiO2 (2.0 g, 55.7 μmol/g) was dispersed in 16 mL of N,N-dimethylformamide (DMF) and n-butyl acrylate (BA) (16.3 mL, 0.114 mol). The solution was added to a 50 mL Schlenk flask and sonicated for 1 min. AIBN (1.14 mL 0.01 M in DMF) was added to the flask, and the solution was degassed by four freeze−pump−thaw cycles, backfilled with nitrogen, and then placed in an oil bath at 60 °C for 3.25 h. The polymerization was quenched by placing the flask in an ice bath. The solution was poured into 120 mL of methanol to precipitate the PBA grafted NPs. The PBA-g-SiO2 was recovered by centrifugation at 5000 rpm for 10 min and redispersed in DMF. The dispersion—precipitation process was repeated another two times. The molecular weight of PBA was measured by using 50 mg nanoparticles in 2 mL of THF with HF (0.2 mL of a 51% solution in water), and the resulting cleaved polymer chains were analyzed by GPC. The cleaved PBA had molecular weight Mₙ = 40 100 and dispersity D = 1.14.

**Synthesis of Poly(styrene-block-(n-butyl acrylate)) Grafted Silica Nanoparticles (PS-b-PBA-g-SiO2).** PBA-g-SiO2 (0.9 g) was dispersed in 20 mL of DMF in a 50 mL Schlenk flask. Styrene (10 mL) was added to the flask and degassed by four freeze−pump−thaw cycles, backfilled with nitrogen, and then placed in an oil bath at 100 °C for 3 h. The polymerization was stopped by placing the flask in an ice bath. The solution was poured into 100 mL of cold methanol, and PS-b-PBA-g-SiO2 was recovered by centrifugation at 5000 rpm for 10 min. This was redispersed in 25 mL of THF, and the dispersion—precipitation process was repeated for another two times. The purified PS-b-PBA-g-SiO2 was dried in a vacuum oven for 24 h. The molecular weight for the block copolymer PS-b-PBA was Mₙ = 50 500 and dispersity D = 1.25.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of PS-b-PBA-g-SiO2.** The RAFT agent CDPA was used for the polymerization of n-butyl acrylate. Thermal-initiated RAFT polymerization of styrene was used to synthesize the block copolymer grafted silica nanoparticles. A series of block copolymer grafted silica nanoparticles with different graft densities and molecular weights were synthesized by using different ratios of monomer to the CDPA terminated PBA-g-SiO2. GPC was used to characterize the molecular weight and dispersity of grafted polymer chains (Figure 2A and Figure S1). In addition, 1H NMR was used to characterize the composition of the block copolymers (Figure 2B and Figure S2). In the 1H NMR spectra, the chemical shift (δ) at 7.09–6.36 ppm was from the aromatic protons of polystyrene while the δ at 4.04 ppm originated from C(==O)O−CH3 in PBA. The ratio of repeat units of styrene and n-butyl acrylate was calculated from the two integrations. TGA was used to characterize the weight percent of silica in the PS-b-PBA-g-SiO2. Higher molecular...
weights resulted in lower silica weight percent with the same graft density and PBA chain length. The characteristic data of the block copolymer grafted silica nanoparticles are listed in Table 1.

**Mechanical Properties of Films Formed by PS-b-PBA-g-SiO$_2$.** Films formed by hot pressing samples of PS-b-PBA-g-SiO$_2$ resulted in transparent matrix-free nanocomposites which were used to characterize the mechanical properties. The stress–strain curves were obtained on dog-bone specimens cut from the films (Figure S3). The ultimate tensile strength, strain at break, modulus, yield strength, and strain are summarized in Table 2. The ultimate tensile stress, strain at break, and modulus varied significantly with changes in graft density and polymer chain length of the PBA and PS.

**Effect of Chain Length on Mechanical Properties.** The films formed by hot pressing of PS-b-PBA-g-SiO$_2$ showed typical properties of thermoplastic elastomers with both elastomeric and plastic behavior (Figure 3A–G). Most of the films with the same graft density and polymer chain length of PBA showed similar trends in mechanical behavior: the ultimate tensile stress increased and strain at break decreased as the corresponding PS chain length increased. Moreover, the elastic modulus increased as the PS chain length increased, which is consistent with typical TPEs.

These relationships were also confirmed by the ultimate tensile stress, strain at break, and modulus versus PS content plots (Figure S4). Luo et al. reported the ultimate tensile strength of TPEs of PS-b-PBA-b-PS increased linearly with PS content at less than 50 wt % PS with the highest stress about 12 MPa. This work introduced the concept of polymers covalently bound to silica NPs, which act as cross-linking sites. However, there was no clear relationship between the silica content and the mechanical properties in the nanocomposites, which was illustrated by the random distribution of points in the ultimate tensile stress vs silica content plot (Figure S4). The yield properties of the films were largely determined by the PS content and the yield strength increased with increasing PS content. All the films with PS content less than 27 wt % did not exhibit yield behavior while the silica content varied from 8.7 to 53.2 wt %. The films with low PS content (BA$_{16k}$-Si$_{12k}$-0.12, BA$_{29k}$-S$_{32k}$-0.24, BA$_{29k}$-S$_{45k}$-0.24, and BA$_{31k}$-S$_{38k}$-0.65) behaved more like elastomers with low elastic modulus. This is likely indicative of the structure with few continuous glassy domains dispersed in the soft PBA matrix. The effect of PBA chain length on the mechanical properties is illustrated in Figure 3H by comparing films with similar PS chain length and the same graft density (BA$_{16k}$-S$_{32k}$-0.24, BA$_{29k}$-S$_{38k}$-0.24, and BA$_{40k}$-S$_{26k}$-0.24). The elastic modulus and yield strength decreased while elongation...
at break increased with increasing PBA chain length. The highest ultimate tensile stress for the TPEs formed by hot pressing PS-b-PBA-g-SiO$_2$ was ca. 17 MPa, which was higher than that reported for TPEs from the triblock copolymer PS-b-PBA-b-PS (ca. 12 MPa) synthesized by RAFT emulsion polymerization.

Effect of Polymer Chain Graft Density on Mechanical Properties. The films formed from grafted NPs with similar graft molecular weights and composition of the block copolymers but differing graft densities (BA$_{42k}$-Si$_{37k}$-0.12, BA$_{40k}$-Si$_{41k}$-0.24, and BA$_{41k}$-Si$_{40k}$-0.65) exhibited similar ultimate tensile stress (ca. 14.0 MPa) and strain at break (150–180% elongation) (Figure S3). The elastic modulus increased as the graft density increased, with 194.9 ± 4.0, 366.8 ± 10.1, and 433.3 ± 13.4 MPa for 0.12, 0.24, and 0.65 ch/ nºm$^2$, respectively. Additionally, all of them showed yielding and the yield strength increased with an increase in graft density. The yield strength was 6.8 ± 0.2, 9.4 ± 0.2, and 12.3 ± 0.6 MPa for 0.12, 0.24, and 0.65 ch/ nºm$^2$ with 43.0, 51.0, and 58.8 wt % PS content, respectively. This indicated there were more continuous glassy domains in the high graft density composites than the low graft density composites.

DSC of PS-b-PBA-g-SiO$_2$. DSC was used to characterize the glass transition temperature ($T_g$) of PS-b-PBA-g-SiO$_2$ with 0.24 ch/ nºm$^2$ graft density and neat block copolymer PS-b-PBA (Figure 4). All the PS-b-PBA-g-SiO$_2$ except BA$_{40k}$-Si$_{40k}$-0.24 showed two clear glass transition temperatures at ca. −44 °C and ca. 106 °C for PBA and PS blocks, respectively. The lack of an observable high $T_g$ for PS in the BA$_{40k}$-Si$_{40k}$-0.24 sample was attributed to the low PS content in the sample. The two distinct $T_g$s indicated microphase separation between PBA and PS in the PS-b-PBA-g-SiO$_2$ samples. There was a single $T_g$ at −47 °C for PBA grafted silica sample PBA$_{40k}$-0.24, which was lower than the $T_g$s of PBA in PBA-b-PS-0.24 samples. The PBA chains in PS-b-PBA-g-SiO$_2$ were restricted by both PS and silica nanoparticles while PBA in PBA-g-SiO$_2$ was merely restricted by silica nanoparticles. This resulted in an increase of $T_g$ of PBA in PS-b-PBA-g-SiO$_2$. The neat block copolymer, PBA$_{40k}$-b-PS$_{21k}$, also showed microphase separation with $T_g$ at −45 and 103 °C. The $T_g$s of polymer grafted silica nanoparticles were slightly higher than the neat block copolymer, which resulted from lower mobility of polymer chains grafted to silica nanoparticles.

SAXS and TEM Characterization. The dispersion state of inorganic nanoparticles in polymer nanocomposites is crucial to their mechanical properties. The dispersion of silica nanoparticles in matrix-free polymer nanocomposites was characterized by SAXS and TEM of micromot films formed by PS-b-PBA-g-SiO$_2$. We used the sample BA$_{40k}$-Si$_{40k}$-0.24 as an example to investigate the dispersion of the silica nanoparticles and microphase separation. The SAXS profile of BA$_{40k}$-Si$_{40k}$-0.24 films showed scattering peaks at 0.126 and 0.316 nm$^{-1}$, which corresponded to domain spacing (d) at 49.9 and 19.9 nm, respectively (d = 2π/λ) (Figure 5A). No higher ordered scattering peaks were observed, which suggested the lack of a highly ordered morphology beyond disordered phase separation. In comparison, the sample of PBA grafted silica nanoparticle BA$_{40k}$-0.24, with the same graft density (0.24
ch/nm²) and molecular weight of PBA, had a scattering peak at 0.290 nm with corresponding d-spacing of 21.7 nm. Krishnamoorti et al. reported that thin films formed by PBA grafted silica nanoparticles with a higher graft density (∼0.8 ch/nm²) showed an ordered liquid lattice with q₁*:q₂* = 1:√3.  

The TEM image of a sectioned BA₄₀k-S₃₉k-0.24 bulk film indicated that silica nanoparticles were randomly dispersed in the matrix-free polymer nanocomposite (Figure 5B). The distances of adjacent silica nanoparticles were analyzed by ImageJ (∼500 distances were analyzed). Statistical histograms and distribution of the interparticle distances were generated from the TEM image (Figure 5C,D). The distribution of interparticle distance showed two peaks at ~25 and ~55 nm, which were close to the two d-spacings (19.9 and 49.9 nm) obtained from the SAXS profile. This indicated the interparticle distances from both TEM and SAXS were consistent with each other.

The DSC measurement of BA₄₀k-S₃₉k-0.24 clearly indicated there was microphase separation of PBA and PS (Figure 4). However, it was difficult to characterize the microphase separation of the block copolymer in the matrix-free polymer nanocomposite by SAXS due to the strong electron density contrast between inorganic silica and the polymers. The strong scattering peaks confirmed the silica nanoparticle dispersion. To eliminate the silica NP effect on the nanocomposite while maintaining microphase separation behavior of the block copolymer, excess HF was used to etch the silica component in the PS-b-PBA-g-SiO₂ film at room temperature. The film after etching showed almost no silica component, which was confirmed by TGA. The original BA₄₀k-S₃₉k-0.24 film formed by hot pressing was transparent with 20.6 wt % silica. The film after etching was semitransparent with 0.5 wt % residual.
Consequently, two weak broad scattering peaks at 0.140 and 0.120, BA40k-S41k-0.24, and BA41k-S40k-0.65, which had similar density for free polymer nanocomposite. Herein we investigated the graft characterization of silica nanoparticles in the matrix—whic were characterized by domain spacings for two scattering peaks representing a longer and shorter distance, with strong peaks at 0.132 and 0.245 nm BA42k-S37k-0.12, BA40k-S41k-0.24, and BA41k-S40k-0.65, exhibited the silica nanoparticles in the BA41k-S40k-0.65 sample, with a higher polymer graft density summarized in Table 3. The higher polymer graft density retained intensity resulted from the electron density contrast derived from phase separation of SiO2 and polymer. The SAXS data of the neat block copolymer PBA48k-b-PS21k exhibited a weak scattering peak at 0.286 nm—1 due to the microphase separation of the blocks (Figure 5A). Thus, the microphase separation of PBA and PS in the nanocomposite BA40k-S39k-0.24 may also contribute to the retained scattering peak after HF etching. The SAXS data of BA42k-S37k-0.65 showed a similar result with weak scattering peaks at 0.139 and 0.343 nm—1 after HF etching, in comparison with strong peaks at 0.132 and 0.245 nm—1 before HF etching (Figure 5S).

Effect of Graft Density on the Silica Nanoparticle Dispersion in Matrix-Free Nanocomposites. SAXS and TEM measurements of the PS-b-PBA-g-SiO2 films were used to characterize the dispersion of silica nanoparticles in the matrix-free polymer nanocomposite. Herein we investigated the graft density effect on the silica nanoparticle dispersion in BA42k-S37k-0.12, BA40k-S41k-0.24, and BA41k-S40k-0.65, which had similar molecular weights of PBA and PS but different polymer graft densities. The SAXS and TGA data of PS-b-PBA-g-SiO2 are summarized in Table 3. The higher polymer graft density resulted in lower silica weight percent in the polymer nanocomposite. SAXS data suggested that all the three samples, BA42k-S37k-0.12, BA40k-S41k-0.24, and BA41k-S40k-0.65, exhibited two scattering peaks representing a longer and shorter distance, which were characterized by domain spacings d1 and d2 (d = 2π/aq). Vaia et al. reported two scattering peaks in a matrix-free polymer nanocomposite film formed by polystyrene grafted (Figure 5E). The SAXS data showed that the two strong scattering peaks disappeared after the silica was etched by HF. This confirmed that these two strong scattering peaks were derived from phase separation of SiO2 and polymer. Consequently, two weak broad scattering peaks at 0.140 and 0.392 nm—1 were retained after SiO2 etching (Figure 5F). This retained intensity resulted from the electron density contrast between PBA and the void space in the film (originated from the pristine silica NP). The SAXS data of the neat block copolymer PBA48k-b-PS21k exhibited a weak scattering peak at 0.286 nm—1 due to the microphase separation of the blocks (Figure 5A). Thus, the microphase separation of PBA and PS in the nanocomposite BA40k-S39k-0.24 may also contribute to the retained scattering peak after HF etching. The SAXS data of BA42k-S37k-0.65 showed a similar result with weak scattering peaks at 0.139 and 0.343 nm—1 after HF etching, in comparison with strong peaks at 0.132 and 0.245 nm—1 before HF etching (Figure 5S).

Effect of Graft Density on the Silica Nanoparticle Dispersion in Matrix-Free Nanocomposites. SAXS and TEM measurements of the PS-b-PBA-g-SiO2 films were used to characterize the dispersion of silica nanoparticles in the matrix-free polymer nanocomposite. Herein we investigated the graft density effect on the silica nanoparticle dispersion in BA42k-S37k-0.12, BA40k-S41k-0.24, and BA41k-S40k-0.65, which had similar molecular weights of PBA and PS but different polymer graft densities. The SAXS and TGA data of PS-b-PBA-g-SiO2 are summarized in Table 3. The higher polymer graft density resulted in lower silica weight percent in the polymer nanocomposite. SAXS data suggested that all the three samples, BA42k-S37k-0.12, BA40k-S41k-0.24, and BA41k-S40k-0.65, exhibited two scattering peaks representing a longer and shorter distance, which were characterized by domain spacings d1 and d2 (d = 2π/aq). Vaia et al. reported two scattering peaks in a matrix-free polymer nanocomposite film formed by polystyrene grafted

![Figure 5. Characterization of the film formed by PS-b-PBA grafted silica nanoparticles. (A) SAXS of BA40k-S41k-0.24, BA40k-0.24, and neat block copolymer BA48k-S21k. (B) TEM image of microtome sectioned film of BA40k-S41k-0.24. The thickness of TEM sample was ca. 100 nm. The yellow lines in the image were the labels used for the interparticle distances analyzed by ImageJ. (C) Histograms of interparticle distances in TEM image. (D) Distribution of interparticle distances. The curve was fitted with Gaussian distribution. (E) TGA data of BA40k-S41k-0.24 before and after HF etching. Inset is the photograph of films before and after etching. (F) SAXS profile of BA40k-S41k-0.24 before and after HF etching.](image)

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</table>

aq represents the ith scattering peak in the SAXS profile. b d = 2π/aq.

silica nanoparticles with 0.05 ch/nm² graft density. As the graft density decreased for the PS-b-PBA-g-SiO2 NPs, the long interparticle distance increased while the short interparticle distance decreased. In addition, the scattering peaks became broader as the graft density decreased, which indicated silica nanoparticles entered into a broader distribution regime. The difference between d1 and d2 in this scenario, can be used to characterize the uniformity of distribution of silica nanoparticles. The Δd = (d1 — d2) was 40.0, 29.8, and 22.3 nm for the graft densities 0.12, 0.24, and 0.65 ch/nm², respectively. This indicated that higher graft densities resulted in a more uniform distribution of silica nanoparticles. The TEM images of sectioned bulk PS-b-PBA-g-SiO2 films showed the silica nanoparticles were randomly dispersed in the matrix-free polymer nanocomposite (Figure 6). The silica nanoparticles in the lower graft density nanocomposite were more densely packed than higher graft density samples. This was due to the higher silica content in lower graft density nanocomposites with 30.5, 20.3, and 9.4 wt % silica at 0.12, 0.24, and 0.65 ch/nm², respectively (Table 3). Despite the differences in the samples, the silica nanoparticles in the BA41k-S40k-0.65 sample, with a high graft density of 0.65 ch/nm², exhibited a more uniform distribution than lower graft density 0.12 and 0.24 ch/nm² samples. DSC and SAXS studies showed microphase
separation, which resulted in different interparticle distances (short and long distances). Nonetheless, the dispersion state of the silica nanoparticles with high graft density was dominated by the steric hindrance of the concentrated polymer brush (CPB) regimes, which resulted in relatively more uniform distribution of silica nanoparticles.33,48,49

We also measured the silica dispersion in approximately monolayer films formed by drop-casting PS-b-PBA-g-SiO₂ THF solution (~0.1 mg/mL) onto a TEM grid. The TEM images of these thin films are shown in Figure 7. For the low graft density 0.12 ch/nm², the distance between silica nanoparticles was 31.1 ± 0.5 nm. As the graft density increased to 0.24 and 0.65 ch/nm², the interparticle distance increased to 38.0 ± 0.5 and 55.9 ± 0.5 nm, respectively, as well as a more uniform silica nanoparticle dispersion. The TEM image of low graft density NPs showed some strings formed in the thin film of BA₄₂k-S₃₇k-0.12. Moreover, the TEM image of BA₄₁k-S₄₀k-0.65 exhibited direct visual evidence of microphase separation of PBA and PS in the polymer nanocomposite (Figure 7C). The black dots in the TEM image were silica nanoparticles, and white corona of silica nanoparticles was PBA while the gray area was PS. This indicated that the PS phase formed a continuous domain, and there were very few entanglements of PBA chains from adjacent silica nanoparticles.

Effect of Graft Density on the Microphase Separation of Polymer in the Nanocomposite. DSC and DMA analyses were carried out to investigate the effect of graft density on the microphase separation of PBA and PS in films formed by BA₄₂k-S₃₇k-0.12, BA₄₀k-S₄₁k-0.24, and BA₄₁k-S₄₀k-0.65. The DSC curves showed that all the three samples had similar glass transition temperatures at ca. −44 °C and ca. 106 °C, which were the Tg's for PBA and PS, respectively (Figure 8A). This indicated that the PBA and PS were microphase separated in each of the samples. DMA, a more sensitive technique for detecting glass transitions, was used to more fully characterize the microphase separation (Figure 8B–D).50 The storage modulus (E'), loss modulus (E''), and dissipation factor (tan δ) are summarized in Table S1. In the storage modulus–temperature curves, all three samples with different graft densities showed a decrease at ~−49 and ~−96 °C, consistent with the Tg's of PBA and PS, respectively. However, they had different PBA glass transition regions at approximately −49 to 50 °C, −48 to 24 °C, and −51 to −19 °C for BA₄₂k-S₃₇k-0.12, BA₄₀k-S₄₁k-0.24, and BA₄₁k-S₄₀k-0.65, respectively (Figure 8B). This indicated that the block copolymer with the highest graft density had better microphase separation of PBA and PS than lower graft densities.51 The rubbery plateau modulus can be related to the number of cross-links or polymer chain length between entanglements.50 The film formed by BA₄₁k-S₄₀k-0.65 had a higher rubbery plateau modulus than BA₄₂k-S₃₇k-0.12 and BA₄₀k-S₄₁k-0.24. The silica nanoparticles can serve as cross-linking points for PBA in the PS-b-PBA-g-SiO₂. The higher rubbery plateau modulus of higher graft density films may result from more cross-links between PBA polymer chains. In the loss modulus vs temperature curves, all the samples showed two peaks at ~−40 and ~−98 °C, which corresponded to Tg's of PBA and PS. However, the Tg peak of PBA became broader when the grafted density decreased from 0.65 to 0.12 ch/nm². In the tan δ vs temperature curves, all the samples exhibited two peaks as for the Tg's of PBA and PS. They had the similar Tg for the PS at ~109 °C. However, they exhibited different Tg for the PBA. The 0.12 and 0.24 ch/nm² samples had similar Tg at ~−29.8 and ~−28.4 °C, respectively, while 0.65 ch/nm² sample had Tg at ~−41.0 °C (Figure S6 and Table S1). Furthermore, the 0.65 ch/nm² sample had a narrow peak for PBA Tg with full width at half-maximum (FWHM) 17.1 °C, which was less than the 0.12 ch/nm² (~81 °C) and 0.24 ch/nm² (43.1 °C) samples. The Tg peaks for PBA became broader when the grafted density decreased from 0.65 to 0.12 ch/nm². All these results indicated a better microphase separation of block copolymers for higher
The proposed model for the graft density effect on the silica dispersion and microphase separation of PBA and PS in PS-b-PBA-g-SiO₂ nanocomposites is illustrated in Figure 9. The TEM images and SAXS data revealed high graft density nanocomposites had a more uniform silica nanoparticle dispersion than low graft density nanocomposites. The DMA data indicated block copolymers with higher graft density in polymer grafted nanoparticles had a better microphase separation than lower graft density when the block copolymers had similar molecular weights and composition. Here the molecular weight of PBA (∼40 kg/mol) was greater than the chain entanglement molecular weight (Mₑ) (∼28 kg/mol).³² At low graft density (0.12 ch/nm²), the NPs appeared to exhibit poor phase separation of the PBA and PS domains, which was confirmed by the DMA studies (Figure 8). The morphology of the corona of the high graft density (0.65 ch/nm²) samples was mainly in the concentrated polymer brush (CPB) regime with highly extended polymer chains.³⁶,⁵³ Thus, it was difficult for the adjacent PBA coronas to entangle with each other, which resulted in a better microphase separation of PBA and PS in high graft density samples as compared to the low graft density samples. This was consistent with the data on particle distribution.

CONCLUSIONS

We prepared a series of thermoplastic elastomers formed by block copolymer grafted silica nanoparticles PS-b-PBA-g-SiO₂ with different chain lengths and graft densities via surface-initiated RAFT polymerization. The effects of polymer chain length and polymer graft density on the mechanical properties were evaluated. The PS content was crucial to the ultimate tensile stress and elastic modulus. An increase in PS content resulted in an increase of ultimate tensile stress and elastic modulus. The longer PBA chain length resulted in a higher strain at break. The higher polymer graft density TPEs had similar tensile strain and stress to the lower graft density TPEs with similar block copolymer chain length. However, the higher graft density TPEs resulted in a higher elastic modulus than low graft density TPEs. The highest ultimate tensile strength of PS-b-PBA-g-SiO₂ (ca. 17 MPa) was higher than the highest value of TPEs from triblock PS-b-PBA-b-PS (ca. 12 MPa) prepared by emulsion RAFT polymerization. DMA, SAXS, and TEM data revealed the higher polymer graft density TPEs had a better microphase separation and more uniform nanoparticle dispersion than lower graft density TPEs with similar polymer chain lengths and composition. This versatile strategy to prepare thermoplastic elastomers by block copolymer grafted nanoparticles broadened the design of new TPEs.
mechanical properties of traditional TPEs formed by ABA triblock copolymers can only be tuned by chain length and composition of the block copolymers. In comparison, TPEs formed by block copolymer grafted nanoparticles introduce a new parameter, polymer chain graft density, as a new tool to enhance microphase separation and hence to tune the mechanical properties of TPEs.

**ASSOCIATED CONTENT**

1. **Supporting Information**
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b00873.

   GPC, $^1$H NMR, and DMA of polymer grafted silica nanoparticles (PDF)

2. **Figure 8.** DSC and DMA characterization of PS-\(b\)-PBA-\(g\)-SiO$_2$ films with different graft densities. (A) DSC curve, (B) storage modulus, (C) loss modulus, and (D) tan $\delta$ of DMA.

3. **Figure 9.** Proposed packing model of low and high graft densities with same polymer chain length and composition of PS-\(b\)-PBA-\(g\)-SiO$_2$ nanocomposite.

4. **REFERENCES**


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**Notes**

The authors declare no competing financial interest.

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