Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polybutadiene Modified Polyaniline Microparticles

Changshu Kuo[a]; Lynne A. Samuelson[b]; Stephen P. McCarthy[a]; Sukant K. Tripathy[c]; Jayant Kumar[d]
[a] Department of Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, USA
[b] U.S. Army RDECOM, Natick, Massachusetts, USA [c] Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, USA [d] Department of Physics, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts, USA

To cite this Article Kuo, Changshu , Samuelson, Lynne A. , McCarthy, Stephen P. , Tripathy, Sukant K. and Kumar, Jayant(2003) 'Polybutadiene Modified Polyaniline Microparticles', Journal of Macromolecular Science, Part A, 40: 12, 1383 — 1396

To link to this Article: DOI: 10.1081/MA-120025317

URL: http://dx.doi.org/10.1081/MA-120025317

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 12, pp. 1383–1396, 2003

Polybutadiene Modified Polyaniline Microparticles[#]

Changshu Kuo,[1] Lynne A. Samuelson,[4] Stephen P. McCarthy,[1]
Sukant K. Tripathy,[2,†] and Jayant Kumar[3,*]

Departments of [1]Plastics Engineering, [2]Chemistry, and [3]Physics,
University of Massachusetts—Lowell, Lowell, Massachusetts, USA
[4]U.S. Army RDECOM, Natick, Massachusetts, USA

ABSTRACT

Polyanionic rubber copolymer microparticles covered with positively charged polyaniline (PANi) as the shell were synthesized. Sodium 4-styrenesulfonate was polymerized in a free radical initiation mechanism in the presence of a low molecular weight hydroxy-terminated polybutadiene (HT-PBD) matrix, which was dispersed in ethylene glycol (EG). Polymerization of aniline monomers was carried out using ammonium persulfate as the oxidant in aqueous hydrochloric acid containing polyanionic rubber copolymer microparticles. The resulting rubber-modified PANi products form a stable and uniform aqueous latex suspension, with a PANi shell loading of 16–58% by weight. From a core-shell microparticle latex suspension containing a PANi loading up to 37% by weight, conductive thin films with good quality can be fabricated by casting. Conductivity of these cast films, after storage for a week in a desiccator, was found to be 0.1 S/cm. These results demonstrated a promising method for the fabrication of conducting polymers with the coexistence of elastic properties in the latex phase of the rubber core and requisite electrical properties of the PANi shell.

Key Words: Polyaniline; Hydroxy-terminated polybutadiene; Sodium 4-styrenesulfonate; Core-shell, Microparticle.

[#] Dedicated to the memory of Professor Sukant K. Tripathy.

[†] Deceased.

[*] Correspondence: Jayant Kumar, Center for Advanced Materials, University of Massachusetts—Lowell, 265 Riverside St., Lowell, MA 01854, USA; Fax: 978-458-9571; E-mail: jayant_kumar@uml.edu.

DOI: 10.1081/MA-120025317
1060-1325 (Print); 1520-5738 (Online)
www.dekker.com

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

INTRODUCTION

The use of conducting polymers requires significant improvements in the mechanical properties of materials for certain applications. The simplest approach to combine electronic conductivity with the desirable mechanical strength of polymers for large-scale applications is a direct blending of conducting polymers, such as polyanilines (PANi), with conventional soluble polymers or thermoplastics.[1,2] However, incompatibility of conducting polymers with the host in a polymer matrix can cause irreversible phase separation or aggregation of microparticles, resulting in significantly reduced conductivities in the final products. The tendency of conductive particles to migrate has created inconsistencies in the electronic performance of these blends, and increased the required percolation threshold for a continuous conducting polymer path. Alternative preparative methods, including in situ polymerizations,[3,4] interfacial polymerization,[5] interpenetrating network (IPN)[6–8] and emulsion polymerization,[9,10] have provided promising approaches in producing technologically valuable blends and composites.

Core-shell copolymer structures with elastic polyurethane cores and PANi shells represent an interesting approach for enhancing processability of bulk elastic materials while retaining low threshold of conductivities.[11] In this paper, we describe a synthetic preparation of a core-shell copolymer-based conducting latex using highly charged poly(sulfostyrene) (PSS)-grafted oligobutadiene as a microparticle core for anchoring the PANi shell. This approach was achieved by polymerization of sodium 4-styrenesulfonate via a free radical initiator in the presence of oligobutadiene diol (PBD), which was dispersed in ethylene glycol (EG). Incorporation of PANi based on the electric charge interaction of aniline monomer is similar to the work reported by Yang.[12,13]

EXPERIMENTAL

General

Sodium 4-styrenesulfonate was purified by dissolving in water first, followed by precipitation from aqueous saturated NaCl. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Aniline was distilled under vacuum and stored under nitrogen before use. Hydroxy functionalized polybutadienediol with a number average molecular weight (M_n) of 2800 was supplied by Aldrich and used as received.

Infrared spectra were recorded as cast films on KBr windows or 3 M IR cards (Type 61, Polyethylene) on a Perkin-Elmer 1720 FT-IR spectrometer. ^{1}H NMR spectra were examined on a Bruker ARX-250 spectrometer. UV-VIS spectra were collected on a Perkin-Elmer Lambda spectrophotometer. Thermogravimetric analyses (TGA) data were measured on a TA Instruments Model 2950 TGA with a heating rate of 10°C per minute. Elemental analyses were carried out at Quantitative Technologies Inc, Whitehouse, NJ.

Synthesis of Polysulfostyrene Grafted Poly(1,4-Butadiene), PSSB1–PSSB4

Preparations of PSS grafted poly(1,4-butadiene) copolymers were carried out at 80°C under N_2 in a 250 mL three-necked flask equipped with a mechanical stirrer. Quantities of reactant and solvent components are summarized in Table 1. A latex-like suspension of hydroxy-terminated poly(1,4-butadiene) (HT-PBD) (2.0 g, M_n 2800) was produced upon vigorous stirring in dioxane–H_2O (4 : 1, 10 mL) and hexane (1.0 mL) containing sodium 4-styrenesulfonate (2.0 g) for the PSSB1 preparation, or in EG (10–20 mL) with or without hexane for the PSSB2–PSSB4 preparation. The AIBN initiator (100 mg) was added at ambient temperature. The reaction mixture was deoxygenated by bubbling a stream of N_2 gas for a period of 30 min. The polymerization reaction began as the temperature was raised to 80°C. After a period of 8.0 h, the reaction mixture was cooled to room temperature. Products were precipitated by the addition of acetone. Removal of residual reactants, organic solvents, and polysulfostyrene (PSS) homopolymer was achieved by dispersing the copolymer products in water (10 mL), followed by the slow addition of acetone until precipitation of copolymer solids. This purification procedure was repeated at least two more times. The resulting PSS-grafted poly(1,4-butadiene) copolymer PSSB4 was further purified three times by solvent extraction with hexane for the removal of remaining free HT-PBD residues. The yield of PSSB1, PSSB2, PSSB3, and PSSB4 was found to be 52%, 74%, 70%, and 65%, respectively. Elemental analyses of PSSB1: C, 47.21; H, 4.55; N, 0.11; S, 12.62. PSSB2: C, 55.37; H, 7.49; N, 0.16; S, 9.05. PSSB3: C, 57.41; H, 7.43; N, 0.09; S, 7.84. PSSB4: C, 48.63; H, 6.14; N, 0.05; S, 11.06.

Synthesis of Polyaniline–Polysulfostyrene Grafted Poly(1,4-Butadiene) Core-Shell Particles, PSSB4–PANi(*n*)

Polymerization of aniline in aqueous latex of PSS-grafted poly(1,4-butadiene) copolymer (1.0 g) was typically carried out at room temperature for a period of 4 h by using a 1 : 1.25 mole ratio of aniline to ammonium persulfate oxidant in dilute HCl solution (0.1 N, 50 mL). The quantity of aniline and ammonium persulfate applied increased from 44 and 135 mg, respectively, for PSSB4–PANi1 to 317 and 970 mg, respectively, for the PSSB4–PANi7

Table 1. Polymerization conditions, the yield, and the ratio of PSS–PBD graft copolymers.

Samples	SS/PBD/AIBN	Solvent	Temp. (°C)	Yield (%)	Product (wt.%) PSS : PBD[a]
PSSB1	2 g/2 g/100 mg	Dioxane : H_2O (80 : 20, 10 mL) Hexane (1.0 mL)	80	52	88 : 12
PSSB2	2 g/2 g/100 mg	Ethylene glycol (20 mL) Hexane (5.0 mL)	80	74	65 : 35
PSSB3	2 g/2 g/100 mg	Ethylene glycol (15 mL)	80	70	57 : 43
PSSB4	2 g/2 g/100 mg	Ethylene glycol (11 mL)	80	65	80 : 20[b]

[a] Determined by elemental analyses.
[b] Treated by solvent extraction.

preparation (detailed conditions are shown in Table 2). The resulting PANi-containing latex was also purified by slow addition of acetone until effective precipitation of the products. Removal of residual reactants was achieved by dispersing the copolymer products in water (25 mL), followed by the slow addition of acetone to effect precipitation of copolymer solids. This purification procedure was repeated twice. Final products of PANi–PSS grafted poly(1,4-butadiene) core-shell particles were kept in aqueous solution. The yields of PANi on PSSB4–PANi1, PSSB4–PANi2, PSSB4–PANi3, PSSB4–PANi4, PSSB4–PANi5, PSSB4–PANi6, and PSSB4–PANi7 samples were 16%, 28%, 37%, 44%, 50%, 54%, and 58% by wt., respectively. Elemental analyses of PSSB4–PANi1: C, 49.18; H, 5.64; N, 2.20; S, 11.09. PSSB4–PANi2: C, 56.86; H, 5.37; N, 3.94; S, 8.48. PSSB4–PANi3: C, 57.51; H, 5.45; N, 5.12; S, 7.33. PSSB4–PANi4: C, 58.53; H, 5.59; N, 6.00; S, 6.46. PSSB4–PANi5: C, 60.30; H, 5.80; N, 6.99; S, 5.61. PSSB4–PANi6: C, 61.76; H, 5.94; N, 7.65; S, 5.25. PSSB4–PANi7: C, 63.04; H, 6.09; N, 8.21; S, 4.80.

RESULTS AND DISCUSSION

Incorporation of PANi in the surface region of sulfostyrene–polybutadiene microparticles was achieved by polymerization of an aniline coating which had been statically attached to the particle in an approach similar to that demonstrated by Yang.[12–15] In order to attract the positively charged aniline monomers and PANi products to the surface of the particle, thus forming a shell structure effectively covering the elastomer core, a great number of negatively charged sulfostyrene grafted on a polybutadiene particle are required. The parent polybutadiene diol (HT-PBD) was synthesized using hydrogen peroxide as an initiator and characterized as consisting of three major terminal hydroxyl moieties as *trans*-PBD—OH, *cis*-PBD—OH, and vinyl-PBD—OH in a relative composition of 48.6%, 16.5%, and 25.2%, respectively.[16] HT-PBD as utilized in this synthesis is of a relatively low molecular weight, with two hydroxyl end-groups. This allowed linear PBD chains to aggregate and form stable suspensions in polar solvents, in particle sizes of roughly 3 to 4 μm as measured by optical microscopy at room temperature. The actual particle sizes involved in reactions at 80°C are believed to be smaller. It was anticipated that there would be dominant distributions of hydroxyl groups at the outer shells of the

Table 2. Polymerization conditions and the yield of PANi on PSS–PBD graft copolymers.

Samples	PSSB4/HCl (0.1 N)	Aniline (mg)	$(NH_4)_2S_2O_8$ (mg)	PANi (wt.%)[a]
PSSB4–PANi1	250 mg/50 mL	44	135	16.0
PSSB4–PANi2	250 mg/50 mL	87	272	28.0
PSSB4–PANi3	250 mg/50 mL	135	412	37.0
PSSB4–PANi4	250 mg/50 mL	181	558	44.0
PSSB4–PANi5	250 mg/50 mL	225	681	50.0
PSSB4–PANi6	250 mg/50 mL	268	822	54.0
PSSB4–PANi7	250 mg/50 mL	317	970	58.0

[a] PANi weight percentages in final products, as determined by elemental analyses.

elastic particles due to hydrophilicity effects, and that these would prove to be the active locations for the grafting reactions. As the anionic sulfostyrene grafting reaction was initiated by AIBN, most free radicals were generated in the hydrophobic phase of PBD. These would then be transferred onto the PBD main chain or styrene sulfonic acid monomer near the interfacial area between hydrophobic suspended microparticles and the EG solution. Copolymerizations continued either by termination reactions of PSS radicals grafting onto the polybutadiene, or the propagation reactions of styrenesulfonic acid monomers initiated by any radical center near the PBD surface. Therefore, the level of PSS grafting correlates to the concentration of effective radicals generated at the interfacial region. The radicals generated inside the hydrophobic microparticles may lead to the radical coupling and the crosslinking reaction of PBD chains, which may also enhance the elastic properties of the low molecular weight PBD microparticles.

Experimentally, EG was found to be the most suitable solvent with a high solubility for both the styrenesulfonate monomer and HT-PBD in the various reaction conditions investigated, as shown in Table 1. Its good compatibility facilitated the formation of a stable and uniform suspension of polybutadiene particles in the polar EG phase. On the other hand, the use of nonpolar solvent (such as hexane) tended to swell and enlarge the HT-PBD particle in size, thus reducing the accessible interface for copolymerization. The high solubility of sodium styrenesulfonate in EG affords better homogeneity of the graft polymer products. There was no significant improvement in terms of solubility by using styrenesulfonic acid without the sodium counter ion. At the end of polymerization, the water-suspended copolymers were isolated and purified by precipitation of the products by acetone dilution for removal of possible poly(styrenesulfonic acid) homopolymer. Unreacted free polybutadiene was removed by repeated hexane extraction from aqueous solutions. The yield of PSS-grafted PBD copolymer was found to be 65–75% with a PSS content in the range of 60–80% by weight depending on different reaction conditions applied. It can be noticed that the numbers of PSS and PBD repeat units in PSSB4 are about the same, even though their weight ratio is 80 : 20. In principle, a higher PSS content leads to attachment of a thicker PANi layer on the core-shell structure, while a higher PBD content affords products exhibiting better elasticity. After purification, the PSSB4 sample was dispersed in H_2O to form a stable homogeneous suspension, indicating an effective surface grafting of PSS on PBD.

The extent of incorporation of PSS moieties was determined by elemental analyses of the sulfur contents in the products, with the corresponding carbon, hydrogen, sodium, and oxygen contents of PSS moieties being calculated based on the sulfur data. The differences of the carbon and hydrogen percentages by weight between the measured values and the calculated values for PSS moieties were determined on the basis of the polybutadiene moieties. Accordingly, the weight ratios between PSS and PBD were elucidated, as shown in Table 1. Proton integration of the products in ^{1}H NMR spectroscopic measurements may provide valuable information regarding the final composition ratios between the different moieties. By utilization of poly(ethylene glycol) as an internal standard for calibration and quantification of sulfostyrene moieties in PSSB4, for example, an estimation of PSSB4 quantity was made and correlated to a PSS vs. PBD ratio of 45 : 55 by wt. This ratio indicates a much lower quantity of PSS in the composition of PSSB4, by comparison with the value of 80 : 20 found by elemental analysis. We interpret this difference in terms of the effective dispersion of a substantial amount of grafted PSS segments in the polybutadiene phase as a gradient core-shell composition. Complications exist since a core-shell particle with an outer hydrophilic shell may prohibit the full detection of all protons inside the hydrophobic core. Apparently, the low mobility of the polybutadiene phase in aqueous (D_2O) reduces the proton detection sensitivity during the ^1H NMR measurement. Meanwhile, due to this gradient core-shell composition, the amount of PSS determined by ^1H NMR should be considered as the effective polyanionic for the subsequent polymerization of aniline in the aqueous solution.

Polymerization of aniline in the presence of core-shell PSS–PBD latex was typically carried out at room temperature by using a 1 : 1.25 mole ratio of aniline to ammonium persulfate oxidant in 0.1 N HCl for 4 h, with reaction conditions summarized in Table 2. The resulting PSS–PBD solids containing PANi were isolated from the latex by adding acetone slowly until precipitation. Repeated purifications were performed by dispersion of core-shell PBD–PSS–PANi particles in water followed by the slow addition of acetone to effect reprecipitation of the products. These core-shell particles can be kept in aqueous suspension for long-term storage without the occurrence of phase separation. In an additional experiment, we found that a small amount of HT-PBD oligomer can be dispersed in the PSS-containing aqueous solution without actually forming any covalent bonding with PSS. Polysulfostyrene macromolecules may serve as surfactants in HT-PBD hydrophobic substances. However, the aggregated dispersion particles were not stable during the polymerization of aniline on treatment by centrifuging. Gradual formation of PSS–PANi complexes at the interface caused disintegration of the latex particles from the surfactants and destabilized the PBD dispersion that resulted in precipitation of PBD solids from the aqueous solution. Therefore, observation of a stable homogeneous aqueous suspension of optimized PBD–PSS–PANi core-shell particles, such as PSSB4–PANi samples containing an appreciable amount of PBD core with a similar number of sulfostyrene and butadiene repeating units, revealed coalescence of PBD and PSS components and the graft-bonding of PSS moieties on the PBD chain.

The infrared spectrum of core-shell PSS–PBD structures, such as PSSB4 in Fig. 1(d), showed characteristic features for both PBD and PSS moieties, with optical absorption of main polybutadiene bands at 967 and 912 cm^{-1} [Fig. 1(b)] and PSS bands at 1010–1300 cm^{-1} [Fig. 1(c)]. A higher absorption intensity of PBD bands than that of PSS bands revealed a relaxed phase of PBD moieties in conjunction with a coagulated phase of charged PSS moieties in the solid core-shell structure. Intense optical absorptions of PSSB4 [Fig. 2(d)] at 1010, 1042, 1129, and 1189 cm^{-1} (corresponding to the stretch of the SO_3 group) have shifted significantly as the PANi incorporation increases from 0 to 58 wt%, while no difference was found at the same bands between PSS [Fig. 2(c)] and PSSB4 [Fig. 2(d)]. This variation of SO_3 vibration energy suggested that complexation of PSS anions with protonated PANi cations became effective at the outer shell region. As a result, the covering of the hydrophobic particle core has also caused the shift of PBD moieties into a condensed phase, displaying a much decreased optical absorption of all PBD bands, as shown in the infrared spectra [Figs. 1(e)–(k)] of all PSSB4–PANi samples.

This unique characteristic of core-shell structures has also been observed in the latexes coated with PANi,[17] poly(3,4-ethylenedioxythiophene) (PEDOT),[18] and polypyrrole.[19] The absorbance intensity of PBD bands at 967 and 912 cm^{-1} was correlated with that of the PSS band at 1046 cm^{-1}, which remained relatively constant upon variation of the PANi content in PANi1–PANi7. As shown in Fig. 3, both peak intensity ratios of I_{912}/I_{1046} and I_{967}/I_{1046} decreased with the increase of the PANi content above 40% by wt. This further

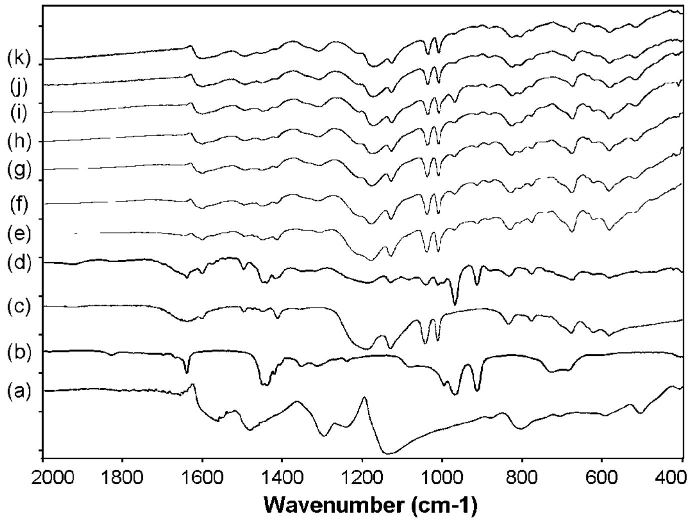

Figure 1. Infrared spectra of (a) PANi; (b) polybutadiene diol (PBD); (c) PSS; (d) PBD–PSS grafted copolymer (PSSB4); and (e)–(k) conductive core-shell microparticles (PSSB4–PANi*n*, $n = 1$ to 7 as shown in Table 2).

provides support for an increasing degree of phase separation of PBD moieties upon the increase of the charge density and the thickness of the external shell.

The frequency of the SO_3 stretching absorption band was found to shift progressively at different degrees as the quantity of PANi incorporated on the core-shell particles increased from 16% to 58% by wt. Complexation of poly(styrenesulfonic) anions with

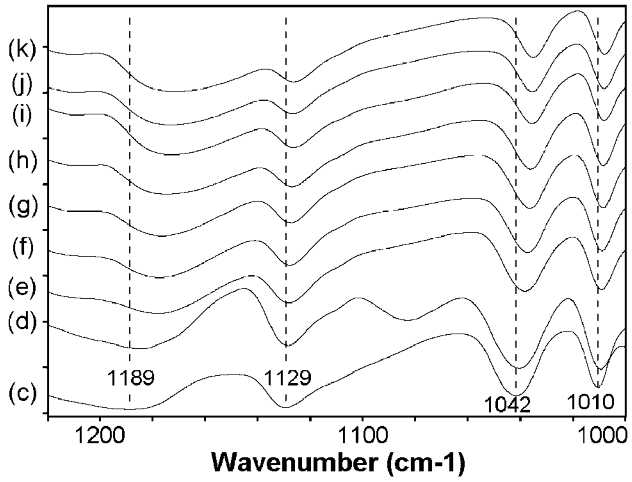

Figure 2. Infrared spectra of (c) PSS; (d) PBD–PSS grafted copolymer (PSSB4); and (e)–(k) conductive core-shell microparticles (PSSB4–PANi*n*, $n = 1$ to 7 as shown in Table 2).

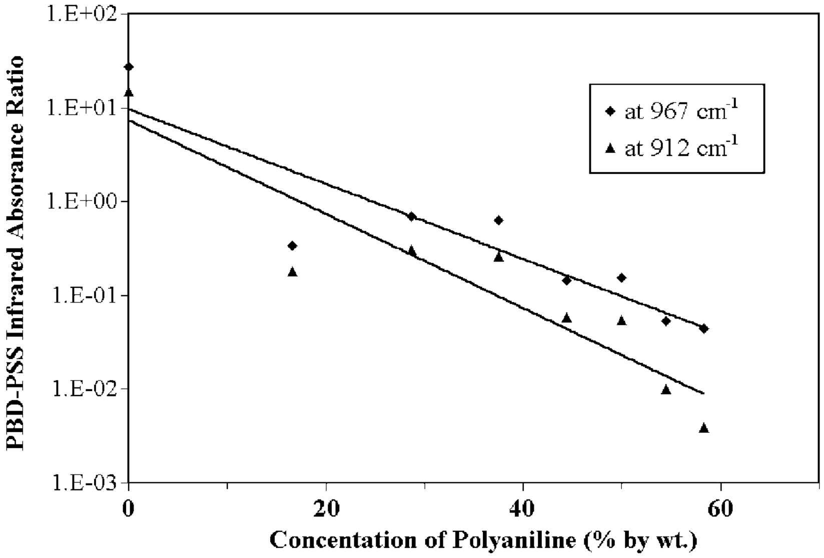

Figure 3. Polyaniline concentration-dependent I_{912}/I_{1046} and I_{967}/I_{1046} ratios of infrared bands corresponding to the absorption of PBD moieties. These decrease with increases of the PANi content from 0 to 60% by wt.

protonated PANi cations may induce the shift, which is very visible at the absorbance frequency of 1189 cm^{-1}. The corresponding shift of the UV-VIS absorption band [Figs. 4(d)–(g)] of quinonoid moieties on samples PSSB4–PANi4 to PSSB4–PANi7 with a higher PANi content was also detected by a cast film on the glass slide. The cationic quinonoid absorption band centered at 750 nm is indicative of the presence of polarons and bipolarons.[20] Strong optical absorption at long wavelengths of 758–780 nm may suggest a continuous conducting phase in all of these core-shell elastic structures that is enhanced by increases in amounts of PANi. Interestingly, the highly polyanilinated core-shell microparticles of PSSB4–PANi7 exhibited a consistently larger optical absorption in intensity at long wavelengths extending beyond 2000 nm, indicating an highly extended charge conjugation along the polymer chain with an improvement of electronic properties of the materials. In order to make solid films with better quality for electrical conductivity measurements, a small amount of isopropanol was added to the PSSB4–PANi aqueous solutions before the casting. The slight swelling of the PBD core induced by the 20% of isopropanol in water may cause uniform shrinkage of both PBD and PANi phases when the cast films were dried at ambient temperature. From aqueous solutions, direct casting films on the smooth surface usually crack after the evaporation of water, especially for samples with high content of PANi. The pressure contact four-point-probe method[21] was employed for the measurement of the conductivity. Without additional doping, conductivities of PSSB4–PANi1 and PSSB4–PANi2 were found to be 1.0 S/cm at ambient temperature. After removal of residual moisture on the films in a desiccator for a period of one week, the conductivity was found to decrease by an order of magnitude, to 0.1 S/cm, which, in fact, is similar in magnitude to that of PSS–PANi complexes without rubber modification.[22]

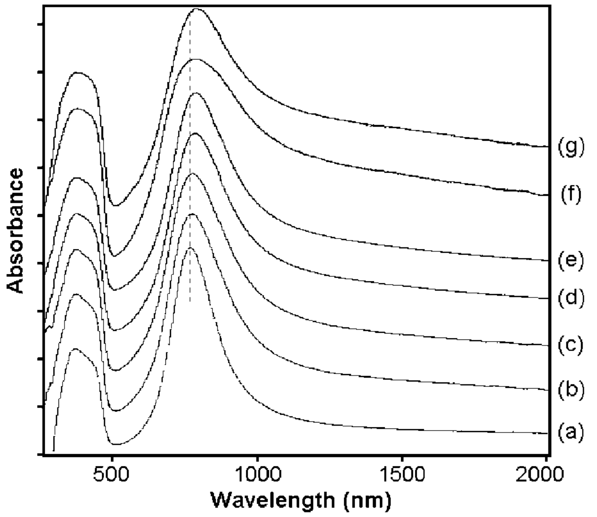

Figure 4. UV-VIS-near-IR spectra of elastic core-shell microparticles, PSSB4–PANi*n* ($n = 1$–7) as cast films on glass slides, indicating extended optical absorptions at long wavelengths.

Examination of the core-shell particle morphology was performed by casting PSSB4–PANi*n* ($n = 1$ to 7) samples on a glass slide from a dilute aqueous suspension for the optical microscopy observations. Figures 5(a) and (b) showed the morphology of the cast sample PSSB4–PANi1 containing 16% by wt. of PANi. With a low loading of PANi on the core-shell structure, a concentration dependency on particle size from 3.0 to 16 μm was observed. Dynamically, PSS–PBD particles were able to aggregate when the interparticle distance is close enough, especially at temperatures far above the glass transition temperature (T_g) of polybutadiene. There is a possibility for the soft flexible segments of polybutadiene to aggregate among particles enhanced at a higher concentration, to form particles with a larger diameter of 16 μm. On the contrary, at a low concentration of 6.5×10^{-5} mg/mL, a smaller particle size of 3.0 μm in diameter was obtained. The distribution of the particle sizes was not homogeneous.

As the loading of PANi increases at the outer shell, the tendency for aggregation of polybutadiene soft segments between particles was significantly reduced, due to improved stability of the particles by fully blocking the PBD core from dynamic merging. Incorporation of more cationically charged PANi may also enhance the intraparticle phase separation of anionic PSS and polybutadiene moieties. Accordingly, a relatively constant particle size of roughly 3.0–4.0 μm in diameter was observed in the case of PSSB4–PANi2 samples [Fig. 5(c)] containing 28% by weight of PANi. The latex particles were stable in H_2O. With further increase of PANi loading to 58% by weight, the proportion of the PBD in the core becomes relatively minor, with PANi complexes being the dominant component of the particle. The core-shell particle size was found to remain small as 4.0–5.0 μm in diameter and stable in the aqueous phase [Fig. 5(d)], even though the distribution of the particle size is slightly larger than that of PSSB4–PANi2.

The thermal stability of these elastic core-shell conductive particles was examined by TGA. As shown in Fig. 6(a), a major weight loss with full thermal degradation of PBD was

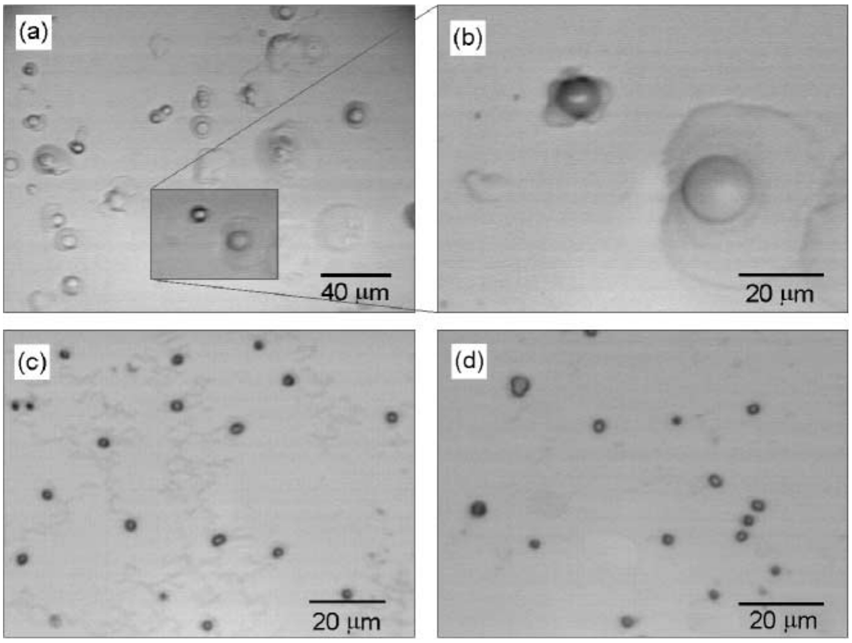

Figure 5. Microscopic morphology of particle samples of (a) and (b) PSSB4–PANi1 with 16% by wt. of PANi; (c) PSSB4–PANi2 containing 28% by wt. of PANi; and (d) PSSB4–PANi7 containing 58% by wt. of PANi, cast from a dilute aqueous solution.

observed to occur at 440°C. A similar thermal degradation also appeared in polybutadiene-containing samples of PSSB4 [Fig. 6(c)] with a much lower percentage of weight loss. Interestingly, the difference in weight loss of PSS [Fig. 6(b)], prepared by a similar procedure described above in the absence of PBD, and PSSB4 at 460°C was found to be roughly 20% by weight, which agrees well with the weight percentage of polybutadiene moieties in the composition of PSSB4 as determined by elemental analysis. An initial weight loss profile of polyaniline-containing PSSB4–PANi1 [Fig. 6(d)] prior to 400°C was consistent with the thermal behavior of PSS–PANi complex which had previously been reported.[23] The overall 45% weight loss of PSSB4–PANi1 at temperatures of 450–700°C was almost the same as that of PSSB4 and remained relatively constant at higher temperature regions, revealing not much further thermal decomposition of aromatics and PANi moieties above 500°C. The thermal stability of the cationic protonated PANi is, generally, lower than its neutral emeraldine base analogs. Accordingly, a more substantial gradual weight loss of 35% below 400°C was detected on the PANi-dominated sample of PSSB4–PANi7 [Fig. 6(e)]. Above 450°C, the thermal stabilities of all core-shell materials became high and comparable.

A weak glass transition temperature of PBD at roughly −90°C was detected on samples of PSSB4 and PSSB4–PANi by differential scanning calorimetry (DSC). Low intensity of the signal is due to the domination of PSS in the materials composition with a minor content of PBD. Elastic characteristics of PBD moieties were better evident in thermal mechanical analyses (TMA), unlike glassy polyelectrolyte PSS which showed

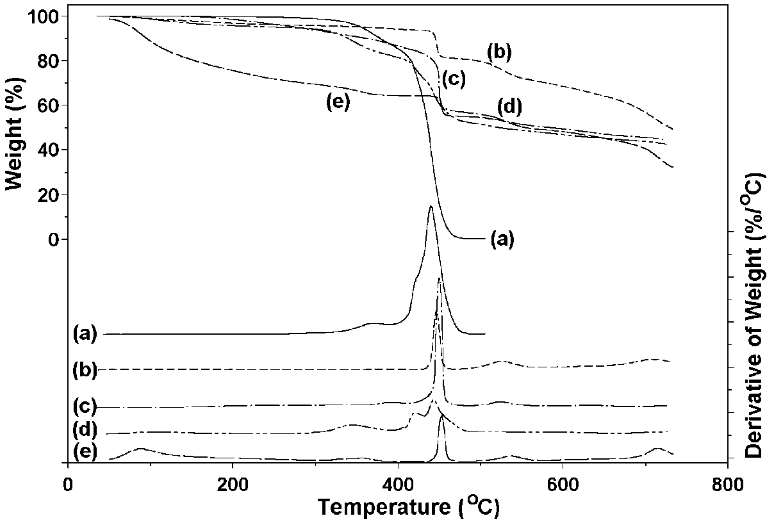

Figure 6. Thermogravimetric analysis of (a) polybutadiene diol (PBD); (b) PSS; (c) the PBD–PSS grafted copolymer PSSB4; (d) PSSB4–PANi1; and (e) PSSB4–PANi7 at a heating rate of 10°C/min under N_2. Polysulfostyrene-containing samples were dried at 100°C under vacuum overnight prior to the measurement.

essentially no significant thermal dimensional change in both penetration and expansion modes of the measurement [Figs. 7(Aa) and (Ba)]. With the incorporation of PBD as the core material, a softening temperature near 45°C was observed in both cases of PSSB4 and PSSB4–PANi1 samples by a penetration probe (Figs. 7Ab and Ac). This softening point, higher than the typical melting temperature of poly(1,4-butadiene) at 2°C indicated a restriction of the PBD soft segment mobility and the shell protection from the PSS and PSS–PANi. In the expansion mode, a clear dimensional change of PSSB4 at a slightly higher temperature (57°C) than that of PSS–PANi1 (36°C) was shown in Figs. 7(Bb) and (Bc), respectively. Retention of rubbery properties of the PBD core was, therefore, substantiated by these TMA results, even though it was covered and blocked by the semi-rigid conductive shell of PSS–PANi complexes. More thermal and electrical properties examined by microthermal analysis and scanning thermal microscopy will be published elsewhere.[24]

CONCLUSION

Conductive PBD–PSS–PANi core-shell microparticles were synthesized in aqueous suspensions. Covalent bonding between PBD rubber and PSS–PANi complex stabilizes the particle and minimizes interparticle aggregation and phase separation. Polymerization of aniline monomers was carried out using ammonium persulfate as the oxidant in aqueous hydrochloric acid containing polyanionic rubber copolymer microparticles. The resulting rubber-modified PANi products form a stable and relatively uniform latex suspension in

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

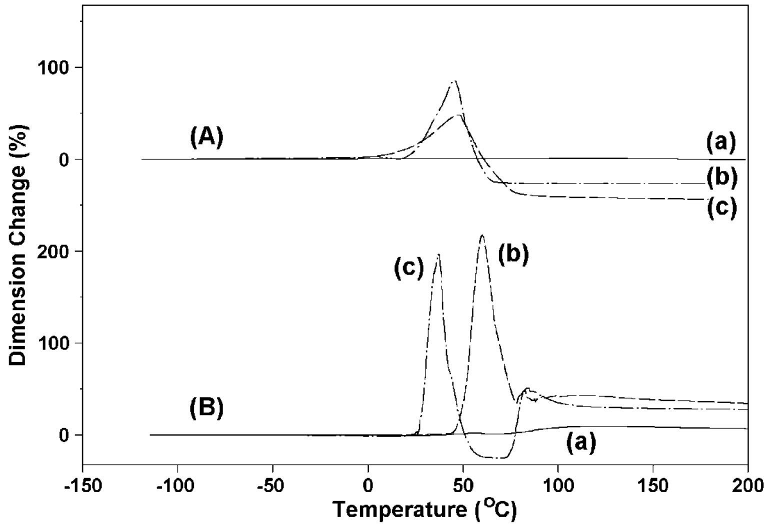

Figure 7. Softening temperatures measured by TMA with (A) penetration probe; and (B) expansion probe with a pressure of 66 psi at a heating rate of 10°C/min under N_2. Film samples of (a) PSS; (b) PSSB4; and (c) PSSB4–PANi1 were dried at 100°C in a vacuum oven overnight.

the reaction solution with a PANi loading of 16–58% by weight. For the latex suspensions with a PANi concentration below 37% by weight, thin films with good quality can be fabricated by simply using a casting method. Conductivity of these cast films was found to be 0.1–1.0 S/cm, which is similar in magnitude to that of PANi–poly(4-styrenesulfonic acid) complexes, without incorporating rubber components. These results revealed a good approach for the fabrication of conductive plastics, showing the coexistence of elastic properties in the latex rubber phase as the core and requisite electronic properties in the rigid phase as the PANi shell. Core-shell structure of the polybutadiene–PANi latex may provide significant advantages with respect to low-temperature processability and improvement in mechanical properties, including impact strength, while maintaining a respectable conductivity.

ACKNOWLEDGMENTS

Dr. Huaibing Liu is acknowledged for his helpful discussions. We also thank Dr. William Bannister for editorial assistance.

REFERENCES

1. Mantovani, G.L.; MacDiarmid, A.G.; Mattoso, L.H.C. Secondary doping in elastomeric polyaniline blends. Synthetic Met. **1997**, *84* (1–3), 73–74.

2. Vallim, M.R.; Felisberti, M.I.; De Paoli, M.-A. Blends of polyaniline with nitrile rubber. J. Appl. Polym. Sci. **2000**, *75* (5), 677–684.
3. Stejskal, J.; Sapurina, I.; Prokes, J.; Zemek, J. In-situ polymerized polyaniline films. Synthetic Met. **1999**, *105* (3), 195–202.
4. Xie, H.-Q.; Ma, Y.-M.; Guo, J.-S. Conductive polyaniline-SBS composites from in situ emulsion polymerization. Polymer **1999**, *40* (1), 261–265.
5. Nakata, M.; Kise, H. Preparation of polypyrrole-poly(vinyl chloride) composite films by interphase oxidative polymerization. Polym. J. **1993**, *25* (1), 91–94.
6. Chiang, L.Y.; Wang, L.Y.; Kuo, C.S.; Lin, J.G.; Huang, C.Y. Synthesis of novel conducting elastomers as polyaniline-interpenetrated networks of fullerenol-polyurethanes. Synthetic Met. **1997**, *84* (1–3), 721–724.
7. Wang, L.Y.; Wu, J.-S.; Tseng, S.-M.; Kuo, C.-S.; Hsieh, K.-H., et al. Synthesis of polyurethane elastomers hypercross-linked by partially hydrated polyhydroxylated C60. J. Polym. Res. **1996**, *3* (1), 1–10.
8. Wang, L.Y.; Kuo, C.S.; Chiang, L.Y. Microscopic surface characterization of polyaniline-based conducting elastomers. Synthetic Met. **1997**, *84* (1–3), 587–588.
9. Osterholm, J.E.; Cao, Y.; Klavetter, F.; Smith, P. Emulsion polymerization of aniline. Synthetic Met. **1993**, *55–57*, 1034–1039.
10. Kinlen, P.J.; Liu, J.; Ding, Y.; Graham, C.R.; Remsen, E.E. Emulsion polymerization process for organically soluble and electrically conducting polyaniline. Macromolecules **1998**, *31* (6), 1735–1744.
11. Bremer, L.G.B.; Verbong, M.W.C.G.; Webers, M.A.M.; van Doorn, M.A.M.M. Preparation of core-shell dispersions with a low Tg polymer core and a polyaniline shell. Synthetic Met. **1997**, *84* (1–3), 355–356.
12. Liu, J.M.; Yang, S.C. Novel colloidal polyaniline fibrils made by template guided chemical polymerization. J. Chem. Soc. Chem. Comm. **1991**, *21*, 1529–1531.
13. Sun, L.; Yang, S.C.; Liu, J.M. Template-guided synthesis of conducting polymers-molecular complex of polyaniline and Polyelectrolyte. Polymer Preprints **1992**, *33* (2), 379–380.
14. Sun, L.; Liu, H.; Clark, R.; Yang, S.C. Double-strand polyaniline. Synthetic Met. **1997**, *84* (1–3), 67–68.
15. Liu, H.; Clark, R.; Yang, S.C. Latex-like water-borne polyaniline for coating applications. Materials Research Society Symposium Proceedings **1997**, *488*, 747–752.
16. Vilar, W.D.; Moutinho, M.T.M.; Menezes, S.M.C.; Coutinho, F.M.B. Characterization of hydroxyl-terminated polybutadiene. V. Structure of polymers produced by thermal and photochemical hydrogen peroxide decomposition. Polym. Bull. **1997**, *38* (3), 319–315.
17. Barthet, C.; Armes, S.P.; Lascelles, S.F.; Luk, S.Y.; Stanley, H.M.E. Synthesis and characterization of micrometer-sized polyaniline-coated polystyrene latexes. Langmuir **1998**, *14* (8), 2032–2041.
18. Khan, M.A.; Armes, S.P. Synthesis and characterization of micrometer-sized poly(3,4-ethylenedioxythiophene)-coated polystyrene latexes. Langmuir **1999**, *15* (10), 3469–3475.
19. Cairns, D.B.; Armes, S.P.; Bremer, L.G.B. Synthesis and characterization of submicrometer-sized polypyrrole–polystyrene composite particles. Langmuir **1999**, *15* (23), 8052–8058.

20. Furukawa, Y.; Ueda, F.; Hyodo, Y.; Harada, I.; Nakajima, T. Vibrational spectra and structure of polyaniline. Macromolecules **1988**, *21* (5), 1297–1305.
21. Frommer, J.E.; Chance, R.R. Electrically conductive polymers. *Encyclopedia of Polymer Science Engineering*, 5th Ed.; Kroschwitz, J.I., Ed.; Wiley: New York, 1986; 462–507.
22. Liu, W.; Kumar, J.; Tripathy, S.K.; Senecal, K.J.; Samuelson, L. Enzymatically synthesized conducting polyaniline. J. Am. Chem. Soc. **1999**, *121* (1), 71–78.
23. Wang, X.; Schreuder-Gibson, H.; Downey, M.; Tripathy, S.K.; Samuelson, L. Conductive fibers from enzymatically synthesized polyaniline. Synthetic Met. **1999**, *107* (2), 117–121.
24. Kuo, C.; Chen, C.-C.; Bannister, W. Microthermal analysis of rubber-polyaniline core-shell microparticles using frequency dependent thermal responses. Thermochim. Acta **2003**, *403* (1), 115–127.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016