Electrically Conductive Polyaniline-Copolymer Latex Composites

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ABSTRACT: We have prepared and characterized a series of polyaniline-copolymer latex composites by chemically polymerizing aniline in the presence of a film-forming chlorinated copolymer latex. The mass loading of polyaniline in the resulting macroscopic precipitates can be easily controlled by varying the initial concentration of the copolymer latex particles. These composites have been characterized in terms of their chemical composition, electrical conductivity, relative thermal stability, and morphology by elemental microanalyses, FTIR microscopy, dc conductivity measurements as a function of temperature, thermogravimetric analysis, and scanning electron microscopy, respectively.

Introduction

Polyaniline is recognized to be an air-stable but unprocessable conducting polymer.[1] Many groups have attempted to improve its processability by various methods including blending with other polymers in cosolvents,[2] synthesizing soluble N- or ring-substituted derivatives,[3-6] preparing sterically stabilized colloidal dispersions,[7-9] or electrochemically polymerizing aniline within a polymer matrix.[10-12] As far as we are aware, there have been relatively few publications concerned with the synthesis of polyaniline (or, indeed, other conducting polymers) in the presence of preformed stable colloidal particles as a route to electrically conducting composites in which the conducting component is well-dispersed within an insulating matrix. Jasne and Chiklis have described an electrosynthesis of polypyrrole in the presence of functionalized latexes to produce conductive composite films which are deposited at the electrode.[13] Dufort et al. have reported a modified approach and claimed both improved mechanical properties and a more uniform chemical composition.[14] Yoneyama et al. have reported the electrochemical preparation of polypyrrole-inorganic oxide films using similar techniques.[15] In 1987 Yassar et al. chemically polymerized pyrrole in the presence of polystyrene latex particles containing surface acid groups to produce composites with conductivities as high as 0.2 S cm^{-1}.[16] More recently Partch et al. have surface-polymerized pyrrole onto inorganic oxide colloids.[17] In this method the chemical oxidant (and hence the locus of polymerization) is *exclusively* situated on the surface of the particles, thus precluding polymerization in the bulk solution. In contradistinction, our own studies of the synthesis of conducting polymers in the presence of large ($\approx$1-μm diameter) silica particles have confirmed that if the oxidant is located in the reaction solution rather than confined to the particle surface a *nonuniform* conducting polymer overlayer coating is formed and concomitant destabilization (precipitation) of the colloidal substrate occurs.[18]

In the present work we have focused on the chemical polymerization of aniline in the presence of a commercial film-forming chlorinated copolymer latex and the characterization of the resulting macroscopic composites.

Experimental Section

The chlorinated copolymer latex (Haloflex EP 252) was supplied by ICI Chemicals and Polymers Ltd. as a 56.5 w/v % dispersion and was used as received. Our photon correlation spectroscopy measurements indicated a particle size of approximately 200 nm,[19] which is in reasonable agreement with the manufacturer's specification of 216 nm. The exact chemical composition of the latex is proprietary but the copolymer contains the following polymerized monomers: vinyl chloride, vinylidene chloride, methyl methacrylate, and butyl acrylate. The minimum film-forming temperature (glass transition temperature) of this latex is 28 °C.

(i) **Preparation of the Polyaniline Composites.** Aniline (0.20 mL) was added to each of eight stirred solutions containing 0.64 g of ammonium persulfate and 0.10-8.41 g of aqueous Haloflex dispersion in 100 mL of 1.2 M HCl at 20 °C. In each case the reaction was left to proceed for at least 18 h. The resulting dark green macroscopic precipitates were filtered under gravity, washed with 1.2 M HCl, and dried in a vacuum oven (60 °C; 10^{-3} Torr) overnight to constant weight. For the electron microscopy and FTIR microscopy measurements (see below) the composites were ultrasonified in 1.2 M HCl, filtered under gravity, washed with copious quantities of 1.2 M HCl, and then dried in a 60 °C oven overnight.

(ii) **Characterization of the Polyaniline Composites.** Room temperature dc conductivity measurements were made on compressed pellets using conventional four-point probe techniques. Conductivity vs temperature measurements were made under dynamic vacuum on the composites utilizing a computer-controlled instrument and thermocouple (10-50-μA constant current source; Hewlett-Packard 3421A data acquisition/control unit). Four-point probe measurements (pressure contacts) were recorded as the cold samples were allowed to warm up to room temperature. FTIR spectra of the polyaniline composites, bulk polyaniline, and the copolymer latex were recorded using a Bio-Rad FTS-40 spectrometer/Digilab IR-400 microsampling accessory (spectral resolution, 2 cm^{-1}; spectral range, 800-1800 cm^{-1}; number of scans, 500-20 000 depending on the sample). A diamond anvil cell was utilized to obtain sufficiently thin "films" ($\sim$1 μm) of the composites. The relative thermal stabilities of the same samples were assessed both in air and under nitrogen using a Perkin-Elmer TGA-7 instrument at a scan rate of 20 °C/min. CHN elemental microanalyses were determined at ICI Chemicals and Polymers Ltd. using a Carlo-Erba 1106 instrument. Scanning electron microscopy studies were made using a Philips

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Table I
Theoretical and Calculated Loading Levels of Conducting Polymer in Polyaniline–Copolymer Latex Composites

sample	theor wt % of polyaniline in composites[a]	microanalyses			calcd wt % of polyaniline in composites[b] (±0.4%)
		C, %	H, %	N, %	
1	5	43.67	5.37	0.10	0.9
2	10	43.90	5.30	0.33	3.1
3	15	44.47	5.27	1.17	11.0
4	20	44.90	5.15	1.33	12.5
5	30	45.63	5.15	2.04	19.2
6	50	47.61	5.01	3.53	33.2
7	60	51.36	5.02	7.18	67.6
8	80	54.12	4.86	9.37	88.2
9	100	55.89	4.90	10.62	100.0

[a] Assuming aniline polymerization goes to completion. [b] Calculated from nitrogen microanalyses.

505 instrument at 30 keV. All scanning electron microscopy samples were sputter-coated with conducting gold overlayers (two 18-mA sputter cycles for 1 min each) to minimize sample charging.

Results and Discussion

The in situ chemical polymerization of aniline to form insoluble polyaniline results in the coprecipitation of the copolymer latex to produce macroscopic composites. We found that by keeping the aniline and oxidant concentrations constant and simply varying the latex particle concentration we could prepare composites of variable polyaniline loadings (see Table I). Since the copolymer latex contained no detectable nitrogen by elemental microanalysis,[20] the polyaniline loading in each of the composite samples was easily calculated from their *reduced* nitrogen content relative to that of bulk polyaniline (N = 10.62%).

For samples 1–6 the actual polyaniline loading was consistently lower than the theoretical loading expected from the synthesis conditions. Our chosen reactant concentrations are 5-fold lower than those usually utilized[21] because such conditions have been shown by Kuhn and Kimbrell to promote *surface* rather than bulk polymerization of conducting polymer monomers on textile substrates.[22] Thus, the lower polyaniline loadings of samples 1–6 probably are a consequence of reduced polymer yields. However, for samples 7 and 8 the actual polyaniline loadings are *higher* than that expected from the synthesis conditions. We believe that this is due to incomplete precipitation of the copolymer latex particles from solution.

Although the actual polyaniline loading is not equal to the theoretical loading for any of the eight samples in Table I, it is nevertheless clear that our synthetic approach enables us to prepare polyaniline–copolymer latex composites which contain variable loadings of the conducting polymer component over the entire composition range.

The relationship between the room temperature electrical conductivity and polyaniline loading level of the eight composite samples is shown in Figure 1. The results indicate typical percolation threshold behavior,[23,24] with reasonably high conductivities being observed even for composites containing relatively low conducting polymer loadings (e.g., sample 5 contains 19.2 w/w % polyaniline and has a conductivity of 0.12 S cm^{-1}). Similar results have been reported by Cooper and Vincent for composite films fabricated from sterically stabilized polyaniline or polypyrrole dispersions mixed with sterically stabilized poly(methyl methacrylate-*co*-butyl acrylate) latex particles.[25] Our results indicate that the polyaniline component is reasonably well-dispersed within the composite, since the observed percolation threshold concentration of 5–10 w/w % is comparable with Cooper and Vincents' results for their polyaniline composites and is appreciably lower than the percolation threshold of 20–30 w/w % observed for their polypyrrole composites. Although we have chosen to express our results in terms of the weight fraction of conducting polymer component in this work, we note that, since the densities of the copolymer latex and bulk polyaniline are so similar (1.60 and 1.50 g cm^{-3}, respectively), the weight fraction of polyaniline is also approximately equal to the volume fraction of this component.

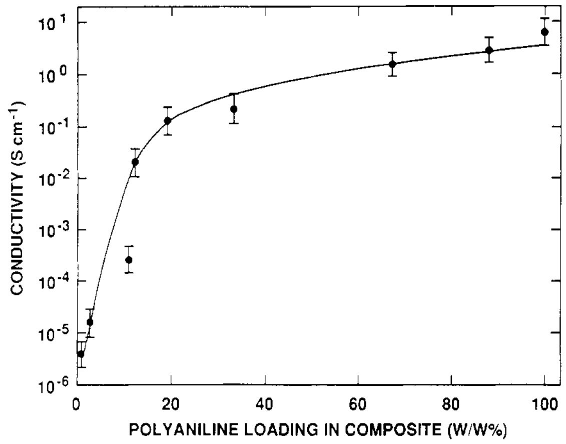

Figure 1. Relationship between polyaniline loading levels and conductivity for the polyaniline–copolymer latex composites.

The dc conductivity temperature dependence of chemically synthesized bulk polyaniline powder has been reported by various groups. For example, Travers et al.[26] examined five polyaniline samples of differing equilibrium pH (doping level) and found that the conductivity, $\sigma(T)$, of the lightly doped samples could be fitted to the Mott–Davies equation for three-dimensional variable range hopping (VRH)[27]

$$\sigma(T) = K_0 T^{-0.50} \exp[-(T_0/T)^{0.25}] \qquad (1)$$

where T is the absolute temperature and K_0 and T_0 are constants. However, for the most heavily doped (highest conductivity) polyaniline sample synthesized using ammonium persulfate oxidant, their data plot of log σ vs $T^{-0.25}$ shows pronounced curvature, indicating that this particular VRH model is inappropriate.

Lundberg and co-workers have shown that a much more linear fit is obtained if log σ is plotted against $T^{-0.50}$.[28] This latter temperature dependence is expected for either a one-dimensional VRH model or a fluctuation-induced tunneling model.[29] Zuo et al. have confirmed the above results for both lightly doped and heavily doped polyaniline.[30,31a] Furthermore, they have interpreted both their thermopower and field- and temperature-dependence conductivity data as evidence that polyaniline is best described as a "granular" or "textured" metal. Very recently Wang et al. have introduced the concept of "three-dimensionality of metallic states" in polyaniline.[31b]

Our dc conductivity temperature dependence studies of two of the composites (samples 2 and 4) and also that of bulk polyaniline over the temperature range 132–287 K are depicted in Figure 2. Like Lundberg et al. we have assumed a one-dimensional VRH mechanism and accordingly plotted log$_e$ (conductivity) vs $T^{-0.50}$. A reasonably linear fit to the data (approximately 400 data points) is obtained for each sample, at least over the temperature range investigated. Composite sample 8, which contains 67 w/w % polyaniline and so lies above the conductivity percolation threshold, exhibited almost identical conductivity–temperature behavior to that of the bulk polyaniline sample. We note that the gradient (T_0) of these

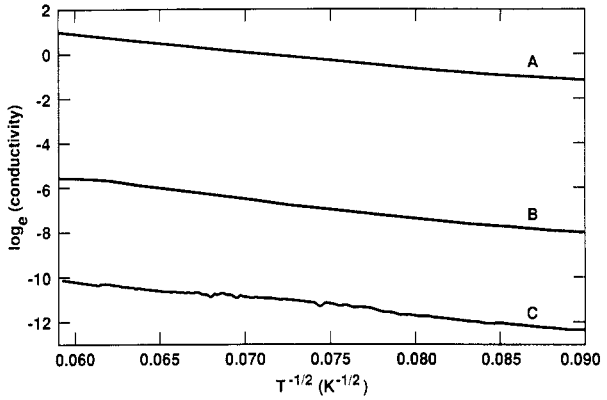

Figure 2. Conductivity vs (temperature)$^{-0.50}$ plots for (A) bulk polyaniline, (B) sample 4, and (C) sample 2.

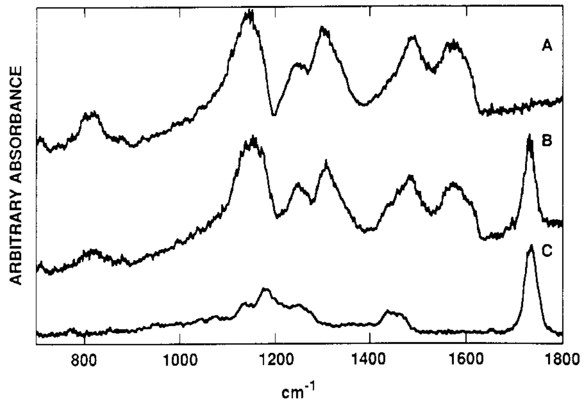

Figure 3. FTIR spectra of (A) bulk polyaniline, (B) sample 4, and (C) copolymer latex.

samples appears to be relatively insensitive to the decrease in conductivity caused by reducing the polyaniline mass loading in the composites. In contrast, Zuo et al. have reported that T_0 is strongly dependent on the doping level (and hence conductivity) of their bulk polyaniline samples.[30,31a]

FTIR spectra of the composites were originally recorded from samples dispersed in KBr disks and were rather unsatisfactory.[20] Our aim in these experiments was to correlate relative peak absorbances of bands due to the polyaniline and copolymer latex components with the known relative mass compositions of the samples as calculated from the elemental microanalyses. Unfortunately, the relative absorbances of the peaks of interest were subject to random fluctuations resulting from the sample pelletization process. However, we obtained better results using an FTIR microscope setup together with a diamond anvil cell to record the spectra of the compressed composite powders directly (see Figure 3). The copolymer latex (curve C) and each of the composites (e.g., sample 4, curve B) has a band at 1732 cm^{-1} due to the ester carbonyl groups of the methyl methacrylate/butyl acrylate comonomers in the copolymer latex, and the absorbance of this peak is compared relative to that of the band at 1580 cm^{-1} due to the polyaniline component (see curve A and ref 1). A plot of relative integrated peak absorbance A_{1580}/A_{1732} vs mass loading of polyaniline (as determined from microanalyses) is depicted for the composite samples 1–5 in Figure 4. The linearity of this relationship suggests reasonable agreement between the *absolute* mass composition calculated from the microanalyses and the *relative* mass composition estimated from the FTIR spectra. The rather low estimate of the polyaniline loading in sample 5 indicated by the vibrational spectroscopy data is possibly related to the unusual morphological changes within this sample (see later). For samples 7 and 8 (containing 67.6% and 88.2% polyaniline, respectively) the ester carbonyl peak was almost completely masked (even with up to 20 000 accumulated scans) by the high background absorbance due to the conducting polymer component. Thus, the A_{1580}/A_{1732} peak integral ratio becomes susceptible to very large errors, and the spectral information obtained is only qualitative at best.

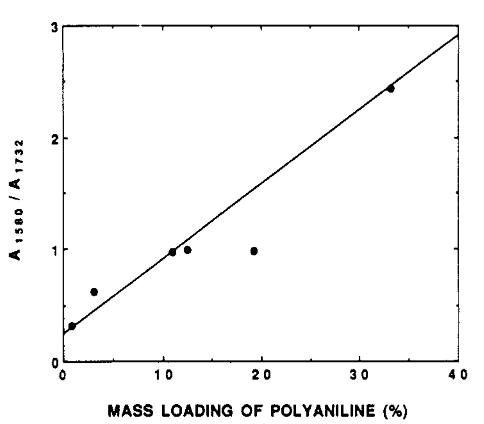

Figure 4. Relative integrated peak absorbance of A_{1580}/A_{1732} bands obtained from FTIR microscopy vs mass loading of polyaniline in composite samples 1–6 as calculated from microanalytical data.

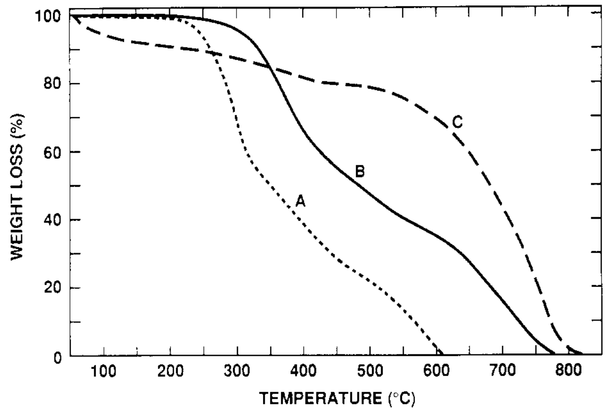

Figure 5. Typical thermograms of (A) copolymer latex, (B) sample 5, and (C) polyaniline. The scan rate was 20 °C/min in air.

In a previous paper we reported that thermogravimetry is a useful technique for the characterization of conducting polymer–silica composites.[18] The relative mass composition of these materials is easily determined from the mass loss due to the volatilization of the conducting polymer component. In the present work the copolymer latex substrate, unlike the silica particles, is volatilized along with the conducting polymer so that the relative mass composition cannot be determined by thermogravimetry. However, this technique still offers a useful guide to the relative thermal stability of the composites.

Our thermal stability studies on the bulk polyaniline sample under an inert nitrogen atmosphere indicate a steady weight loss above ambient temperature, culminating in a relatively high residues content of 51.5% at 615 °C. This result is consistent with the work of both Wei and Hsueh[32] and Traore et al.[33] In contrast, the copolymer latex was more stable at lower temperatures, with no detectable weight loss up to 210 °C, but decomposition was complete by 615 °C with no residues remaining. The composite samples showed intermediate behavior with the residue mass at 615 °C ranging from 2.24% (sample 1) up to 43.0% (sample 8).

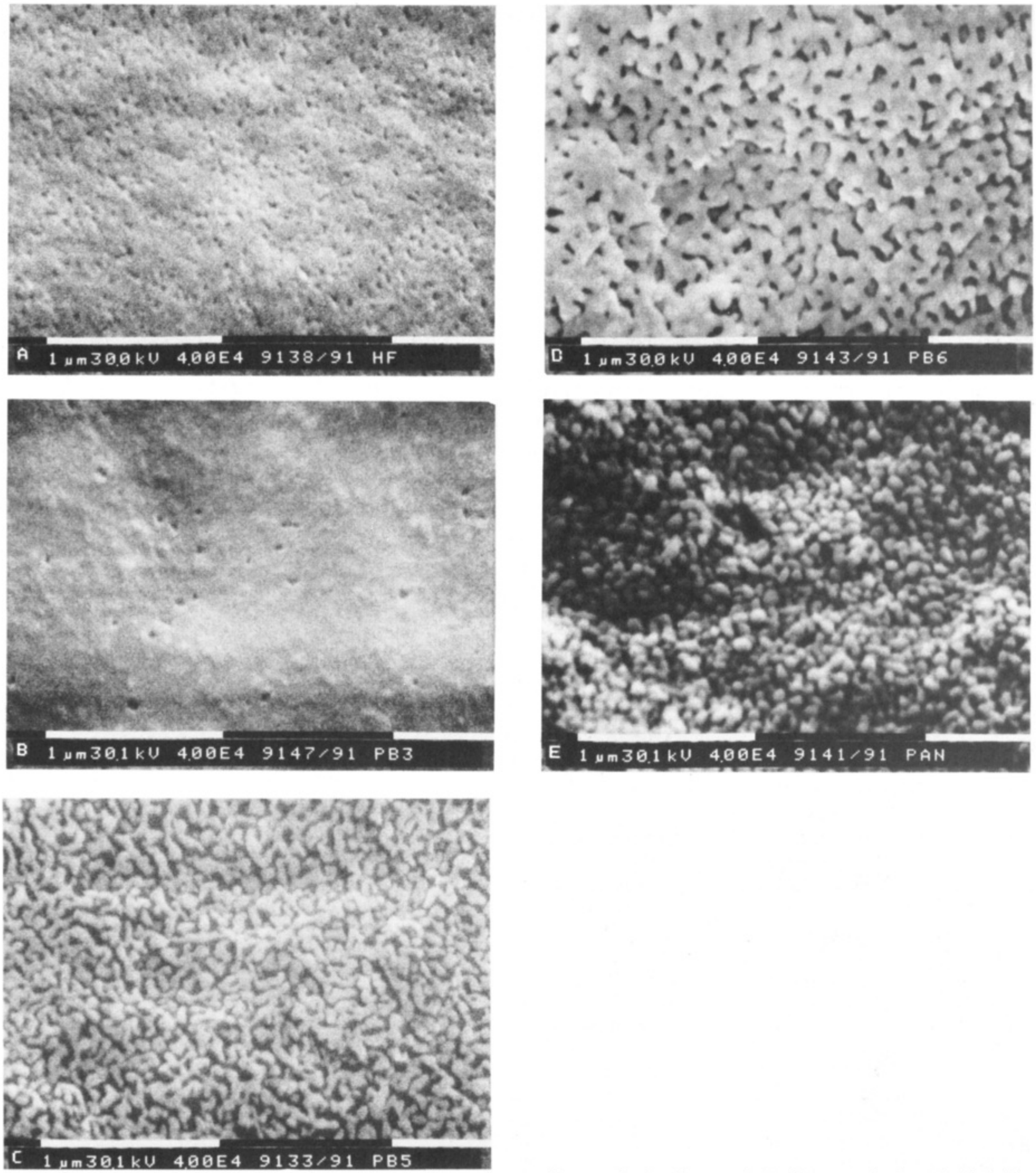

Figure 6. Scanning electron micrographs of (A) copolymer latex, (B) sample 3, (C) sample 5, (D) sample 6, and (E) bulk polyaniline.

In Figure 5 we see the thermograms of the copolymer latex, bulk polyaniline, and composite sample 5 run under an ambient atmosphere. The copolymer latex is stable up to approximately 200 °C, whereas the bulk polyaniline sample exhibits discernible weight loss at temperatures as low as 60 °C due to loss of water and HCl. Remarkably, composite samples 1–5 (only sample 5 is shown for clarity) all appear to be significantly more stable than either the copolymer latex or the bulk polyaniline powder, with almost negligible weight loss up to 250 °C. The enhanced stability of these samples may be related to the ability of the water-impermeable copolymer latex to act as a sealant and so prevent small-molecule (e.g., H_2O, HCl) elimination at elevated temperatures. The morphology of the composites may also significantly influence their thermal stabilities (see below). We note that composite samples 6–9, which contained smaller proportions of the copolymer latex component, exhibited thermal stabilities more similar to that of the bulk polyaniline sample.

A series of scanning electron micrographs all taken at the same magnification (see 1-μm scale bar) are depicted in Figure 6. In Figure 6A we see the featureless morphology of the film-forming copolymer latex. Clearly the low T_g of the latex has ensured efficient particle coalescence and the individual primary particles (originally 200-nm diameter) are no longer discernible. In Figure 6B the morphology of composite sample 3 is very similar to that of the copolymer latex, but in Figure 6C (sample 5) we observe a remarkable "worm-like" morphology. A globular, fused morphology is evident in Figure 6D (sample 6), and finally in Figure 6E we see the polydisperse spherical morphology (average particle diameter 50–100 nm) of bulk polyaniline powder prepared in the absence of the copolymer latex. This latter morphology is very similar to that previously reported by Wessling and Volk for chemically synthesized polyaniline.[34] Thus, these electron microscopy studies confirm the dramatic morphological changes occurring within the composites as the relative mass loading of the polyaniline component is increased. These results are in contrast with those reported by Yassar et al. for polypyrrole-coated polystyrene latexes.[16] In this latter system the higher T_g of the polystyrene latex substrate (~104 °C) prevents particle coalescence and the individual spherical composite particles are easily visible by scanning electron microscopy. More direct comparisons between these two systems are difficult since Yassar et al. did not report the relative polypyrrole–polystyrene mass composition for their composite samples.

In general, our scanning electron microscopy studies confirm that the polyaniline component is homogeneously distributed throughout the composites down to submicronic length scales. Clearly, our colloidal approach is well-suited to the facile preparation of conducting polymer composites over a wide compositional range with a high degree of dispersion of the conductive component within an insulating matrix.

Conclusions

We have shown that polyaniline–copolymer composites can be easily prepared by chemically polymerizing aniline in the presence of a copolymer latex. The mass loading of the polyaniline component in such composites may be determined from the nitrogen content of the composites and can be readily controlled over a very wide range (0.9–88.0 w/w %) by simply varying the initial copolymer latex concentration. The conductivities of our composite samples indicate typical percolation threshold behavior with a percolation concentration of approximately 5–10 w/w %.

Plots of $\log_e \sigma$ vs $T^{-0.50}$ for the temperature dependence of the conductivities of these composites are approximately linear over the temperature range 132–287 K. This is consistent with either a one-dimensional variable range hopping model or, alternatively, a fluctuation-induced tunneling model. Our FTIR microscopy studies of the composites provide an unambiguous semiquantitative confirmation of the polyaniline–copolymer latex relative mass composition. These results are fully consistent with those obtained from CHN microanalyses. The relative thermal (oxidative) stabilities of some of the composites (samples 1–5) are superior to that of either the individual polyaniline or copolymer latex components run under identical conditions. Our scanning electron microscopy studies confirm that the polyaniline component is well-dispersed within the composites and clearly reveal remarkable morphological changes within the composites as the mass loading of polyaniline is increased.

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