In situ Synthesis of Polyaniline in Poly(dimethylsiloxane) Networks Using an Inverse Emulsion Route

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Polyaniline (PANI) was successfully prepared in end-linked poly(dimethylsiloxane) (PDMS) networks using an inverse emulsion method. Its generation as dispersed particles was confirmed by UV/Vis spectrophotometry, Fourier transform infrared spectrometry, scanning electron microscopy and energy dispersive X-ray analysis. The content, particle sizes and degrees of dispersion of the PANI particles were studied with regard to the pore dimensions of the PDMS networks, which had known cross-link densities. Variables such as the nature of oxidants, solvent contents, solubility parameters, miscibility properties, and chemical interactions, etc. were also investigated, and a possible reaction mechanism was proposed.

Keywords polyaniline, poly(dimethylsiloxane) networks, inverse emulsions, cross-link densities

Introduction

Electrically conducting polymers have received a great deal of attention over the past three decades. Most such polymers belong to the category of polyenes or polyaromatics, examples being polyaniline, polyacetylene, polypyrrole, polythiophene, poly(*p*-phenylene), poly(phenylene vinylene), etc. These new generation polymers show great potential in various technological applications, such as sensors, batteries, electrochemical displays, catalyst, antistatic coatings, anticorrosive coatings, electromagnetic shielding, functional membranes, controlled release of ionic drugs, etc. Among them, polyaniline (PANI) has been studied most extensively because of its relatively high conductivity, easy preparation from low cost raw materials, relatively low density, excellent environmental stability, and relatively easy processability.[1,2] However, much effort will be required to make PANI practically useful in these applications. These required efforts include:

First, increasing conductivity. Highly ordered PANI and higher charge-carrier mobility could be expected from confining PANI into layered materials.[3] Higher

conductivity may also be achieved by doping PANI with carefully chosen reactants and reaction conditions, such as the types and concentrations of dopant, oxidant, solvent, etc.[4−7]

Second, obtain processability improvement by increasing solubility in common organic solvents or water. Introducing alkyl or alkoxy chain into the *meta-, ortho-*position of the aniline ring or N-position of PANI, give the possibility of enhancing solubility in organic solvents. For example, synthesis of both ring and N-sulfonated PANI was shown to help with regard to dissolving PANI in water.[2,8]

Another goal is to obtain novel or synergistically-improved mechanical, electrical, optical, thermal, and magnetic properties by preparing polymer blends or polymer composites. These could contain conductive polymers and a variety of other components, including polymer hosts, metals, low molecular weight inorganic and organic materials, etc.[2,3,9−19] For example, chiraloptical properties were obtained by preparation of PANI using an electron acceptor 2,3-dichloro-5,6-dicyanobenzoquinone as oxidant and camphorsulfonic acid as the dopant and the chiral inductor.[9] PANI salts have also been used as catalyst supports in the hydrogenation of 2-ethylanthraquinone.[10]

PANI could be incorporated into such other components using mechanical mixing, in-situ polymerization, copolymerization or grafting methods. Various specific techniques are available, including electrochemical polymerization, chemical polymerization, photochemical polymerization, methathesis polymerization, plasma polymerization, pyrolysis, etc. Chemical polymerization attracts more attention since it could be used to prepare large amounts of PANI at low cost. Also, PANI could be generated on the surface of other materials by bulk chemical polymerization or surface polymerization, and could also be penetrated into micro- and nano-structured materials (silicon, carbon, silica, zirconia, titania, copper oxide, clays, zeolites, . . .).[1−19]

A recently developed chemical polymerization method, an "inverse emulsion" route, used the oil-soluble oxidant benzoyl peroxide (BPO), the emulsifier sodium lauryl sulfate (SLS) and solvents such as chloroform to maximize PANI content. The materials were dispersed in hydrophobic PDMS networks instead of using traditional routes, which use water-soluble oxidants such as $(NH_4)_2S_2O_8$, H_2O_2, $FeCl_3$, $KMnO_4$, $K_2Cr_2O_7$, $KClO_3$, $KBrO_3$, KIO_3, etc.[2−8,10−19] In these studies, UV/Vis spectrophotometry, Fourier transform infrared spectrometry, scanning electron microscopy, and energy dispersive X-ray analysis were used to characterize the PANI and the PANI-PDMS composites.

Up to now, there have been very few reports on the preparation of PANI in polymer networks.[18,19] It would be particularly important to have results on the effects of a polymer matrix with controlled cross-link densities (pore sizes) on the properties of in-situ prepared PANI and its composites.

In this paper, we report the *in situ* synthesis of a PANI salt in poly(dimethylsiloxane) (PDMS) networks which were formed by careful end linking of hydroxyl-terminated polymer chains. Number-average molecular weights between crosslinks were taken to be the same as that of the polymer precursor (4200, 18,000, and 36,000 g/mol). This variation was used to evaluate the effects of network pore size on the PANI particle contents, sizes and degrees of dispersion. Other variables such as monomer/oxidant ratio and amounts of solvent were considered, and a reaction mechanism was proposed.

Materials

The samples of hydroxyl-terminated PDMS with the number-average molecular weights cited, the crosslinker tetraethoxysilane (TEOS) $[Si(OCH_2CH_3)_4]$, and stannous octoate

(STO) catalyst were purchased from Gelest, Inc. The monomer aniline (at least 99.0% pure), the oxidant benzoyl peroxide (BPO), the emulsifier sodium lauryl sulfate (SLS) and solvents such as chloroform, acetone, and N-methyl pyrrolidone (NMP) were obtained from the Aldrich Chemical Co. All of these chemicals were used as received, without further purification.

Preparation of the PDMS-PANI Composites

End-linked PDMS networks were prepared, in the usual manner, with TEOS as the multi-functional end linker and STO as the catalyst.[20–22] Scanning electron microscopy showed that the crosslinked networks were void free. A portion of the crosslinked PDMS with approximate dimension of $10 \, mm \times 10 \, mm \times 30 \, mm$ was swelled in a solution containing 6.05 g BPO and 25 ml chloroform for 24 h.

Samples of PANI salt and PANI composites were synthesized using a method similar to that reported elsewhere,[4–8,14–17] but in the presence of a portion of PDMS network swelled with the BPO solution. Specifically, in an Erlenmeyer flask, 2.25 g of the emulsi-fier SLS dissolved in 25 ml of water, and 50 ml of aqueous 1 M HCl, were added to the chosen amounts of aniline and chloroform. To this milky white emulsion solution, the pre-viously prepared PDMS network swelled with the BPO solution was added. The solution was magnetically stirred at room temperature for 10 min. The remaining BPO chloroform solution was then added dropwise through a separatory funnel with continuous stirring over a period of 0.5 h. The resulting polymerization reaction was carried out at room temp-erature for 24 h, as the milky white emulsion solution gradually became dark green. In order to break the emulsion and precipitate the PANI, 200 ml of acetone was then added to this solution and set aside for 24 h. The PDMS-PANI composites, along with some samples of pure PANI, were obtained by filtration. The products were slowly dried in a fume hood for 48 h, followed by vacuum drying for 48 h.

In this paper, PDMS4200-PANI2.5 indicates the PDMS-PANI composites prepared using PDMS with number-average molecular weight 4200 g/mol and 2.5 ml aniline monomer.

UV/Vis Spectrophotometry

PANI samples were dissolved in dilute solutions with NMP in order to measure the UV–Vis transmittance at room temperature. This was done on an HP 8453 UV–visible spec-trometry (Hewlett-Packard GmbH, Waldbornn, Germany), over a range of 300–900 nm.

Fourier Transform Infrared Spectrometry

The transmission FTIR spectra of PANI salt, uncrosslinked PDMS, crosslinked PDMS network, and PDMS-PANI composites cut from the edge areas (which were dark green) were recorded on a Perkin-Elmer Spectrum One spectrometer (Perkin-Elmer Cetus Instru-ments, Norwalk, CT) in the range of $4000–450 \, cm^{-1}$. Small pieces of sample (0.2 g) were ground into powders and mixed homogeneously with potassium bromide (KBr) and their IR spectra recorded.

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis

The samples of PDMS-PANI composites were sectioned in a manner to ensure that the microstructure remained intact. The fractured surfaces were then mounted on aluminum

stubs and sputtered with 60% Au/40% Pd. Scanning electron microscopy was performed using a Hitachi S-4000 microscope with a field emission source. Accelerating voltages in the range between 2 and 10 KeV were used to minimize sample charging during imaging. Images in the secondary mode were captured at fixed magnifications using a digital image capture system. An Oxford Instruments detector was used in combination with ISIS software to perform energy dispersive spectroscopy (EDS) on the samples. An accelerating voltage of 10 KeV was found to be suitable for the EDS analysis as this provided sufficient X-ray excitation energies while keeping charging and beam damage to a minimum.

Results and Discussion

Electronic Absorption Spectra

Relevant here is the fact that PANI chains are rigid, *para*-linked phenylene amineimine structures, and are available in various forms depending on the degree of oxidation and the degree of doping. In the presence of protonic acid, chemical oxidative polymerization of aniline generally involves PANI salts. PANI salts can be converted into PANI base by de-doping with sodium hydroxide solution.[7] PANI base can be denoted as $[(-B-NH-B-NH-)_y(-B-N=Q=N-)_{1-y}]_n$, where B denotes a $-C_6H_4-$ ring in the benzenoid form and Q denotes a C_6H_4 ring in the quinoid form. $1-y$ describes the content of oxidized units. Leuco emeraldine base is a type of polymer which has no oxidized units, thus $1-y=0$, while the pernigraniline base is a fully oxidized form of the polymer, with $1-y=1$. Emeraldine base denotes a kind of half-oxidized polymer, which has equal numbers of oxidized units and reduced units, with $1-y=0.5$.

Generally, various forms of PANI base are insulators, while the emeraldine salt is the only conductive form.[19] In a sense, the molecular structure of PANI parallels those of some classes of important polymers. Specifically, the rigid-rod polymers have some bulky and thermally stable aromatic groups in their backbones, particularly arylene groups (such as *para*- and *meta*-phenylene, diphenyl ether, etc.), and alkarylene groups (such as *meta*-xylylene, etc).[23−25] These polymers have advantages such as thermal stability, stiffness, etc. They also have the disadvantages of infusibility, insolubility and incompatibility with other polymers, which have restricted many of their applications.

PANI salt is not soluble in most of the organic solvents except possible slight solubility in dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and NMP. In this paper, the electronic absorption spectrum of PANI was obtained by dissolving PANI salt in the NMP solution, with the results shown in Fig. 1. The results are similar to those in the literature.[4−9,14−17] with two broad electronic absorption bands, with one around 310–350 nm and the other around 620–660 nm. The first band is assigned to the π-π^* transition of the amine and the latter to the excitation of the imine units of the PANI backbone.

Infrared Spectra

The infrared spectra of PANI salts and various polysiloxanes have been extensively reported in the literature,[3−8,12−17,26−30] making possible reliable assignments of transmittance peaks. Figure 2a shows the infrared spectrum of PANI salt prepared in the presence of PDMS4200, with vibrational bands at 3419.8, 3230.0, 2900.0, 1685.2, 1569.0, 1499.2, 1384.4, 1293.5, 1240.0, 1099.1, 800.3, 707.7, 505.6 cm^{-1}. The broad band centered at 3419.8 cm^{-1} is assigned to the NH asymmetric stretching vibration of the $C_6H_4NHC_6H_4$ group. The band at 3230.0 cm^{-1} is assigned to the symmetric stretching
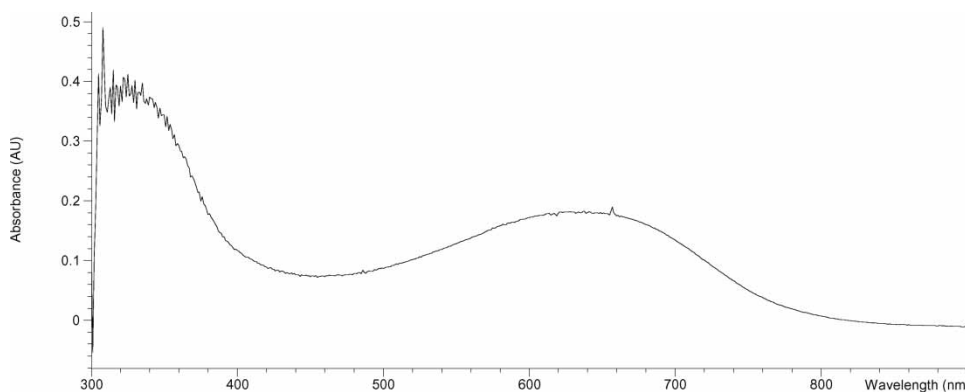
Figure 1. UV–Vis spectra of the PANI HCl salt obtained in NMP.

of the NH_2^+ group and is a indication of protonation of the PANI salt. The peak at $2900.0\,cm^{-1}$ could be due to the –CH stretching vibration of the aromatic ring, and the band at $1685.2\,cm^{-1}$ may indicate carbonyl groups formed (since BPO also initiates the free radical reaction of C–H and forms carboxyl acid in the presence of oxygen). The bands at 1569.0 and $1499.2\,cm^{-1}$ could be attributed to ring stretching vibrations associated with quinoid and benzenoid forms, respectively, and the bands at 1384.4 and $1293.5\,cm^{-1}$ could be due to C–N stretching vibrations of QBQ, QBB, and BBQ. The band at $1240.0\,cm^{-1}$ is assigned to C–N asymmetric stretching vibrations of the aromatic amine, and the strong band at $1099.1\,cm^{-1}$ is due to aromatic C–H in-plane bending modes. The C–H out-of-plane bending mode has been used to explain the band at $800.3\,cm^{-1}$. The ring C–C bending vibration was observed at $707.7\,cm^{-1}$, and the ring in-plane deformation was at $505.6\,cm^{-1}$.

Figure 2b shows the infrared spectrum of uncross-linked PDMS4200 (with 8% TEOS). It shows the characteristic peaks of PDMS, such as (1) the silanol peak around $3432.4\,cm^{-1}$, (2) the asymmetric and symmetric CH_3 stretching preaks centered at 2963.7 and $2904.5\,cm^{-1}$, (3) a strong peak indicating CH_3 bending modes at
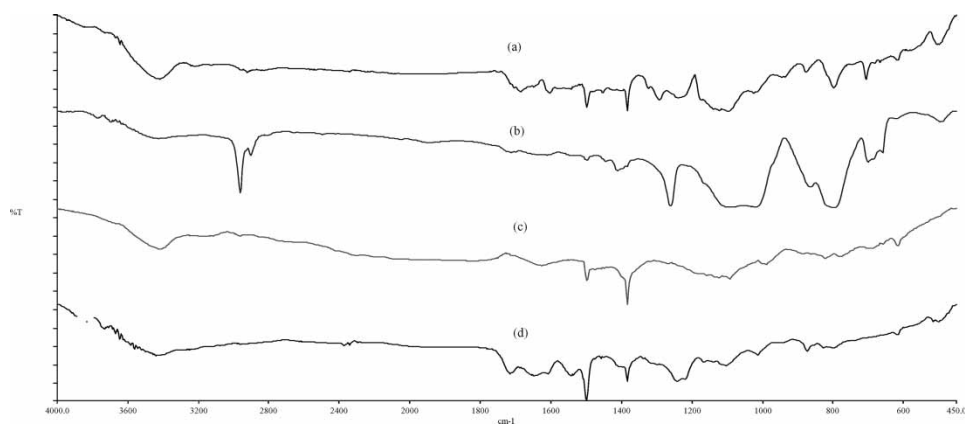

Figure 2. FT-IR spectra: (a) PANI salt (HCl), (b) uncross-linked PDMS4200, (c) cross-linked PDMS4200, (d) edge area in the PDMS4200-PANI2.5 sample.

$1262.0\,\text{cm}^{-1}$, (4) a strong and broad peak at $1090.2\,\text{cm}^{-1}$ assigned to asymmetric Si−O−Si stretching, and (5) a strong Si−C stretching and asymmetric CH$_3$ rocking peak at $801.5\,\text{cm}^{-1}$.

The infrared spectrum of cross-linked PDMS4200 (with 8% TEOS) is shown in Fig. 2c, with the new peak at $1384.3\,\text{cm}^{-1}$ indicating ethoxylated PDMS. The band centered at $3419.4\,\text{cm}^{-1}$ characterizes silanol groups formed during the hydrolysis of TEOS. Figure. 2d shows the infrared spectrum of the edge (dark green) area in the PDMS4200-PANI2.5 sample. The broad band centered at $3444.0\,\text{cm}^{-1}$ should be the combined effects of silanol groups and the NH asymmetric stretching vibration of the C$_6$H$_4$NHC$_6$H$_4$ group. The peaks at 1717.5 and $1650.7\,\text{cm}^{-1}$ may indicate carbonyl groups formed, and the peak of quinoid stretching is shifted to a lower wavelength of $1543.9\,\text{cm}^{-1}$ (in comparison with that of PANI at $1569.0\,\text{cm}^{-1}$). The stretching vibrations peak for the benzenoid forms has no shift and occurs at $1500.0\,\text{cm}^{-1}$. There are also the expected (1) peak for the C−N stretching vibrations at $1384.50\,\text{cm}^{-1}$, (2) the C−N asymmetric stretching vibrations of the aromatic amine at $1242.70\,\text{cm}^{-1}$, (3) the overlap peaks of aromatic C−H in-plane bending modes, and (4) the asymmetric Si−O−Si stretching at $1104.60\,\text{cm}^{-1}$.[3−8,12−17,26−30]

Particle Sizes and Degrees of Dispersion

The method of forming networks by end linking chains was chosen here to give elastomers of known structure,[20,21] to be used to estimate the effects of increasing chain length on the *in situ* generated PANI. The *in situ* polymerization of the aniline monomer in the PDMS network has to be constrained by the nanosized spaces or pores defined by the chains between the crosslinks. Relevant in this regard are some representative SEM micrographs of the cross-sectional surfaces of PDMS-PANI composites shown in Fig. 3. There is seen to be a general trend of the PANI content and particle sizes increasing with decreasing degree of crosslinking. In other words, the PANI content and particle sizes increased with increase in the molecular chain lengths of PDMS chains (increase in the network pore dimensions). This is somewhat complicated by the fact that the size distributions of the particles were broad, with diameters ranging from several hundred nanometers to tens of micrometers. Similarly broad size distributions were observed in the in-situ precipitation of silica into *trans*-1,4 polybutadiene networks.[31,32] They might result from several effects. First, the solubility parameters of PDMS and aniline are probably different enough that immiscibility could cause the formation of at least some relatively large droplets of aniline solution forming within the PDMS networks. In fact the immiscibility of PANI with other polymers is known to be one of the major drawbacks limiting its applications. Such effects might be enhanced by the fact that chemical interactions between the PDMS elastomer and the PANI domains might be very weak since PANI has no appropriate functional groups.

The inhomogeneities caused by the immiscibility are of interest, as is illustrated by some of the results presented in Table 1. The dark green color of PANI concentrated in the edge area could be easily distinguished from the transparent areas toward the center having little PANI. The nature of the PANI particles formed obviously depends on the pore dimensions of the PDMS networks (as gauged by the molecular weights between cross links). SEM indicates that in the center area of PDMS4200 the sizes of PANI are about tens of nanometers to hundreds of nanometers. In the case of the higher molecular weight PDMS18000 and PDMS36000, the sizes are larger, from hundreds of nanometers to several micrometers.[31]

As expected, an increase in the amount of aniline monomer or chloroform solvent increases the thickness of the edge area in the composites, as shown in Table 1. It is plausible to assume that increase in the amount of aniline would increase the amount of PANI generated, and increase in amount of chloroform would help transport the aniline
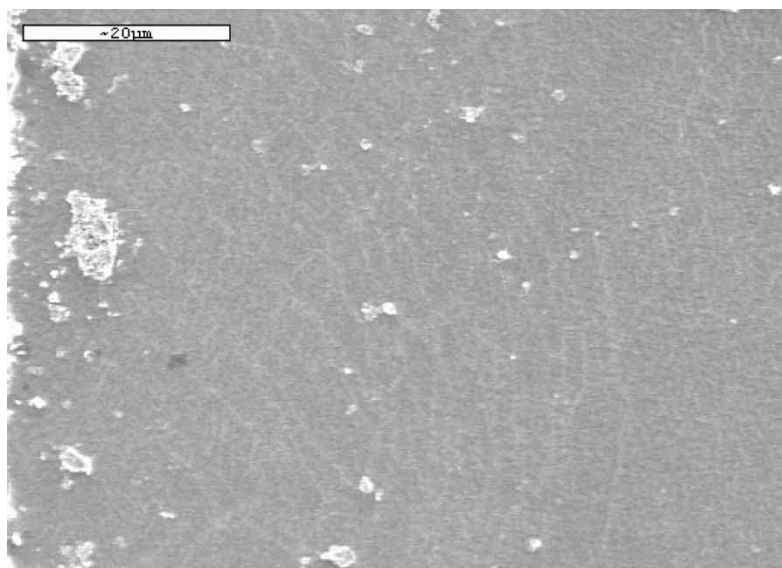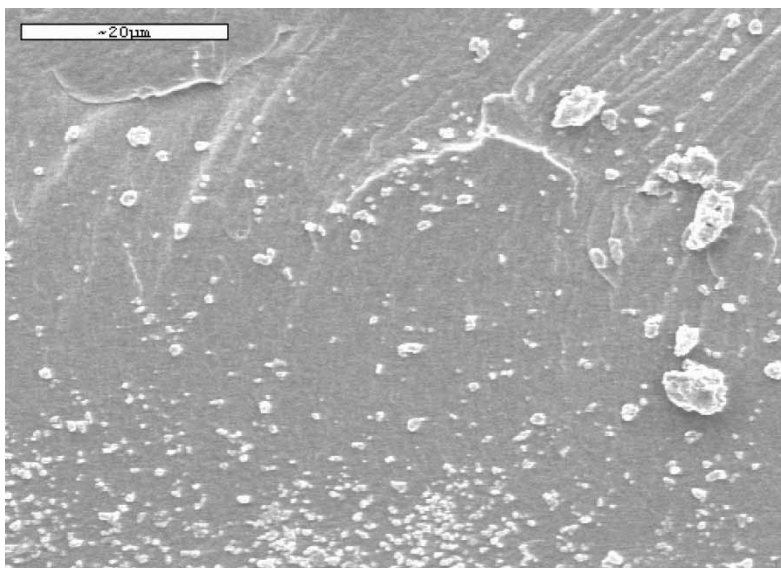

(a)
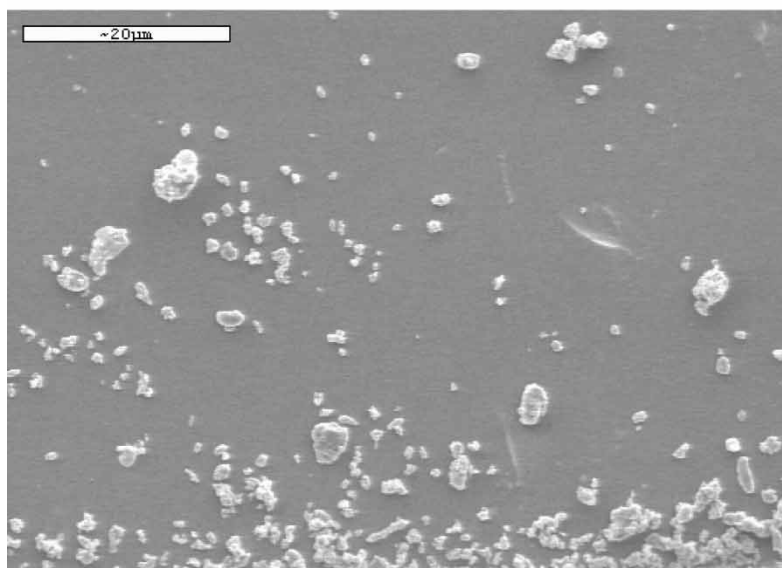
(b)

Figure 3. Scanning electron microscope images showing the edge areas of PDMS-PANI composites: (a) PDMS4200-PANI2.5, (b) PDMS18000-PANI2.5, (c) PDMS36000-PANI2.5.

(c)

Figure 3. Continued.

and oxidant BPO to deeper regions of the PDMS networks. However, SEM micrographs of the edge areas of the composites shown in Fig. 4 and elsewhere[31] do not support this simplest interpretation. Increase in amounts of aniline from 1.5 ml to 2.5 ml did increase PANI content and particle sizes in the PDMS18000 networks. However, further increase in amounts of aniline to 3.7 and 4.8 ml, gave the opposite effect. Similar results were observed in the case of increase in amounts of chloroform.[31] For example, 75 ml chloroform solvent would generate large PANI particles in the edge area PDMS18000 networks that were larger than those prepared using 50 ml chloroform. However, 100 ml chloroform solvent generated only a very small number of large clusters.

Rao and Sathyanarayana synthesized PANI in the presence of the dopant sulfosalicylic acid, using a similar technique. They reported the conductivity and yield of PANI

Table 1
Measured thicknesses of some sample edge areas

	Total thickness (mm) of edge areas in PDMS-PANI composites						
	50 ml Chloroform			75 ml Chloroform		100 ml Chloroform	
ml of Aniline	PDMS 4200	PDMS 18000	PDMS 36000	PDMS 4200	PDMS 18000	PDMS 4200	PDMS 18000
1.4	2.30	5.74	5.92	2.90	6.17	NA	9.38
2.5	2.78	6.10	6.44	4.10	9.40	6.42	NA
3.7	2.81	5.89	6.47	4.10	9.45	4.10	9.42
4.8	2.90	7.55	7.43	NA	7.00	NA	NA

synthesized depended on the concentration of the oxidant BPO. Jeevananda et al. studied the inverse emulsion polymerization of PANI doped with *p*-tolulene sulphonic acid at 60°C using the same oxidant BPO. They also found the concentration of BPO affected both the yield and conductivity of the PANI obtained. Both quantities increased with increase in BPO concentration but only up to a critical value, with decreases beyond it.[4,17] They attributed this to an over oxidation of PANI to its non-conducting form above this critical
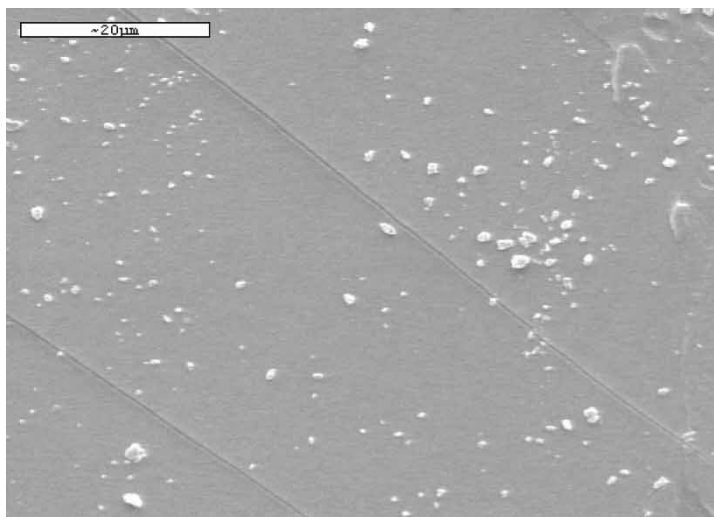
(a)
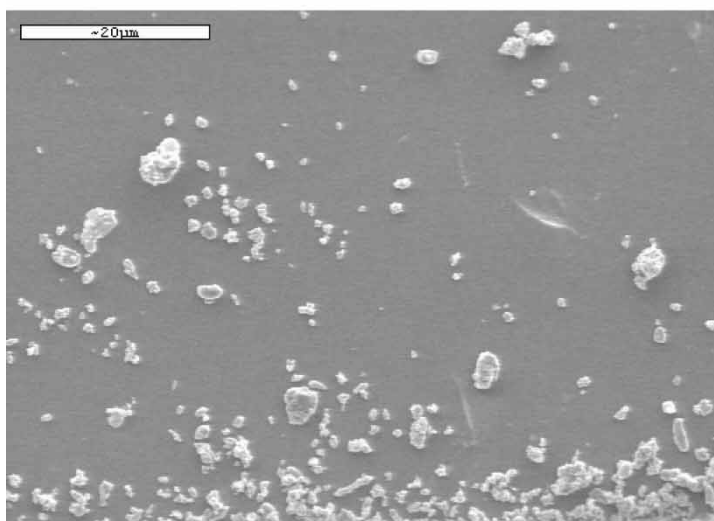
(b)

Figure 4. Scanning electron microscope images show the edge areas of PDMS-PANI composites: (a) PDMS18000-PANI1.15, (b) PDMS18000-PANI2.5, (c) PDMS18000-PANI3.7, (d) PDMS18000-PANI4.8.

(*continued*)

(c)

(d)
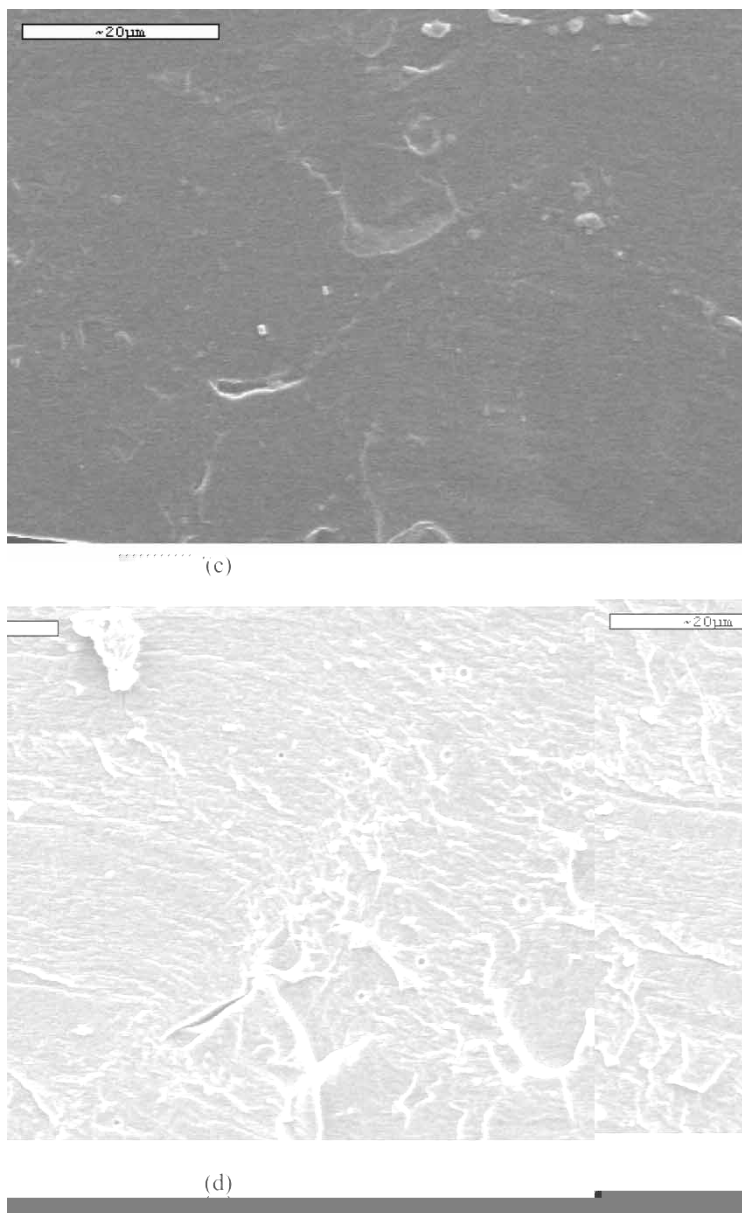
Figure 4. Continued.

concentration of oxidant. Similar results were observed in the present study, as shown in Table 2. The optimal oxidant concentration in our system seems between 1.4–2.5 ml, since the PANI yield would decrease beyond this, and the nonconducting form of PANI would be generated in the PDMS. This is consistent with the smaller amounts of PANI observed in the edge areas in the PDMS18000 networks, for aniline amounts larger than 3.7 ml. The same may be true with regard to the chloroform concentrations, since large amounts of it could also give the non-conducting form of PANI.

Table 2
PANI yields from various amount of aniline and chloroform[a]

	Yield of PANI (%)		
ml Aniline	50 ml Chloroform	75 ml Chloroform	100 ml Chloroform
1.4	87.7	88.2	85.0
2.5	89.0	76.9	75.4
3.7	68.3	60.6	59.4
4.8	49.7	52.7	69.5

[a]Aniline density taken to be $1.02 \, g/ml$ at $20°C$.

Reaction Mechanism

Relevant here are the EDAX results on the PDMS elastomer and PANI composite particles comprising the PDMS18000-PANI2.5, as presented in Fig. 5. The numerical elemental compositions of PDMS matrix and PANI particles of PDMS18000-PANI2.5, PDMS36000-PANI2.5 are shown in Table 3. As can be seen, carbon weight percentages are much higher in PANI composite particles than in the PDMS matrix, indicating the particles are indeed primarily PANI. It should be pointed out that EDAX can qualitatively describe the elemental distribution of the composite samples, but could not provide very precise information on sample composition because the beam scattered during the scanning measurements. Also, some of the elements' peaks overlapped, such as those from carbon and nitrogen.

The results, however, do suggest a possible reaction mechanism for this in situ synthesis of PANI in PDMS networks. The PANI is preferentially generated around the elements sodium, stannous tin, and chlorine. The emulsifier SLS is the source of the sodium, and the STO provides the tin and both are amphipathic, comprised with hydrophobic segments (aliphatic groups) and hydrophilic segments (metal salts). Also the SLS helps to transport the BPO, aniline, HCL, and water into the PDMS matrix. This gives the inverted emulsion, with the oily droplets containing the hydrophobic oxidant BPO, chloroform, and some of the amphipathic aniline transported through the SLS monolayer. These oily droplets are apparently preferentially formed around the STO (with its hydrophobic aliphatic groups 2-ethylhexanoate and hydrophilic stannous salt). Thus, polymerization takes place in these oily droplets, and the PANI particles formed after precipitation would contain some sodium and stannous elements. The significant amounts of sodium, stannous, and chlorine elements in the PANI particles could also be due to the electrical properties of the electrically conductive PANI salt doped with the HCL. The strong electron-withdrawing nature of the chlorine could provide chloride anions to ionically couple with PANI cations. SLS containing anions of aliphatic sulphate acid and sodium cations and STO containing anions of aliphatic acid and stannous cations, could also form some ionic interaction with the PANI salt.

Future work could elucidate the broad size distributions of PANI particles resulting from the differences in solubility parameter, the immiscibility and absence of strong chemical interactions between the PANI (or aniline monomer) and the PDMS networks. Specific approaches could be:
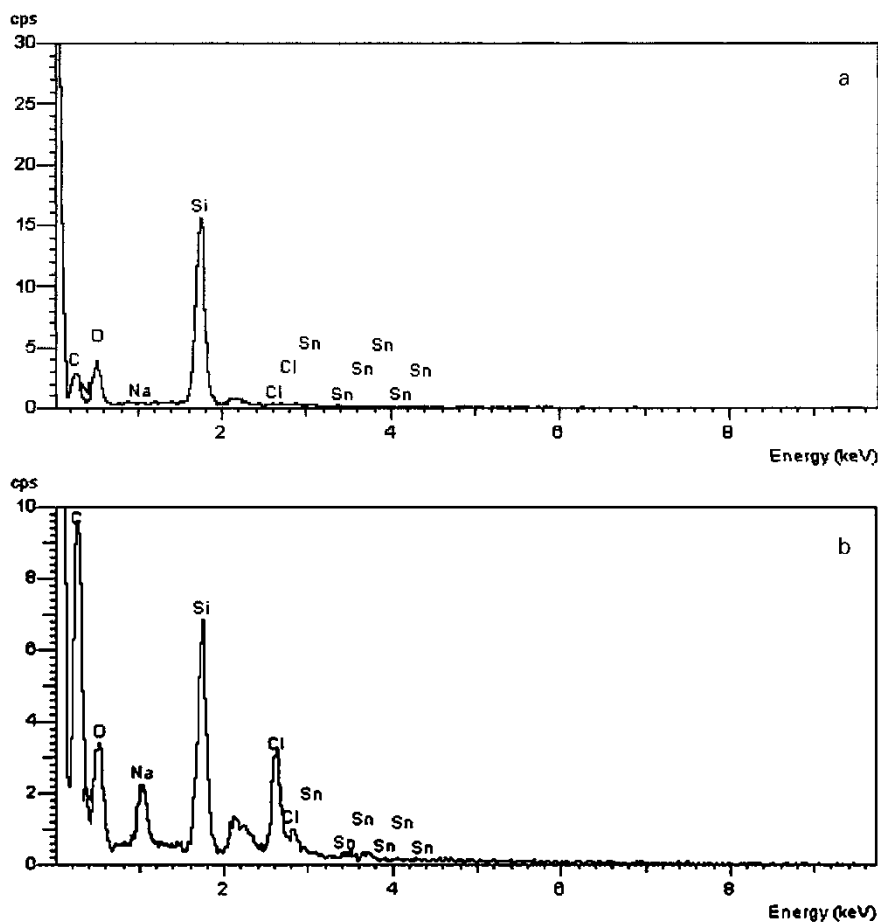
Figure 5. EDAX results for the PDMS matrix (a) and PANI composite particles (b) in PDMS18000-PANI2.5.

1. Introduction of aromatic or larger R aliphatic groups into the molecular structures of functionally-terminated PANI or polysiloxane, such as poly(methylphenylsiloxane), poly(diphenylsiloxane), diphenylsiloxane-dimethylsiloxane copolymers, etc.
2. Selection of cross-linking agents other than TEOS, preferably with aromatic or other larger R aliphatic groups.
3. Use of silane-coupling agents, or incorporation of a variety of functional groups into the elastomer or the PANI.

Conclusions

The amounts, particle sizes and degrees of dispersion of PANI particles were studied as a function of the pore sizes of end-linked PDMS networks of known crosslink density. Also characterized were the effects of oxidant, solvent, solubility parameters, miscibility, chemical interactions, etc. A variety of characterization methods confirmed the successful *in situ* preparation of PANI in PDMS networks and suggested a possible reaction polymerization mechanism.

Table 3

Elemental compositions[a] for PDMS matrix and PANI particles in
PDMS18000-PANI2.5 and PDMS36000-PANI2.5

	Element weight percentages for PDMS matrices and PANI particles			
	PDMS18000		PDMS36000	
Element	PDMS matrix	PANI particles	PDMS matrix	PANI particles
C	2.65	41.01	NA	55.73
N	1.86	14.03	NA	NA
O	34.97	21.87	28.26	11.66
Si	60.52	11.01	71.74	12.22
Na	NA	3.19	NA	0.79
Sn	NA	NA	NA	NA
Cl	NA	8.89	NA	19.59
Total	100.00	100.00	100.00	100.00

[a]From EDAX analyses for two crosslink densities.

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