Composites of Electronically Conductive Polyaniline with Polyacrylate−Silica Hybrid Sol−Gel Materials

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A series of new composite materials that consist of electronically conducting polyaniline and polyacrylate−silica hybrid sol−gel network have been prepared via the sol−gel reactions of the precursor polymer, poly[methyl methacrylate-*co*-3-(trimethoxysilyl)propyl methacrylate], in the presence of camphorsulfonic acid-doped polyaniline in *m*-cresol solution. These materials as coatings can be tailored by varying the composition to have an excellent adhesion to inorganic substrates such as silica glass and indium−tin oxide and a reasonably high conductivity. The adhesion and durability of the new composites as the electroactive coatings on indium−tin oxide electrode are much superior to those of the conventional polyaniline system under repeated electric potential cycling conditions. The modulus of the composite films was also found to be relatively greater than that of the polyaniline films.

Introduction

In the past two decades, electronically conducting organic polymers, such as polyaniline, polythiophene, polypyrrole, polyacetylene, polyphenylenevinylene, etc., have emerged as a new class of materials.[1,2] Intensified basic research has revealed a broad spectrum of potential commercial applications of this class of materials in electronic, optical, biological, and other civilian/defense industries.[1,2] Particularly, some conducting polymers, e.g., polyaniline and its derivatives, exhibit interesting electrochromic and corrosion-inhibiting properties.[3,4] There is a major drawback when the conducting polymers are to be used in the coating applications that involves interaction of the conducting polymers with other types of inorganic substrate materials such as glass, ceramics, metals, etc.: the incompatibility of these organic conducting polymers with the inorganic materials, as reflected by the poor adhesion and low bonding strength of the polymers to the inorganic surface, which in turn lead to poor stability and durability of the coatings. Recently, we have developed a new general methodology that could incorporate virtual any conventional vinyl polymers into inorganic (e.g., silica) networks via the sol−gel process.[5−7] We envisioned that if the sol−gel precursors, e.g., poly[methyl methacrylate-*co*-3-(trimethoxysilyl)propyl methacrylate] [P(MMA-MSMA)] and/or tetraethyl orthosilicate (TEOS), can be introduced into the conducting polymers, new polymer systems should be attainable to have enhanced adhesion and bonding strength between the conducting polymers (e.g., polyaniline) and the inorganic substrates without a significant loss of the desired electronic properties of the conducting polymers. Since these systems are composite materials of the conducting polymers with organic−inorganic hybrid and/or silica network in nature, it is perceivable that they could be fabricated into desirable solid objects such as parts, films, fibers, coatings, etc.

In this paper, we present the first successful preparation of the new composite materials of conducting polyaniline with polyacrylate−silica hybrid sol−gel network. P(MMA-MSMA) was employed as the sol−gel precursor in this study. The materials were characterized by infrared spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). In addition to the synthesis of the new materials, we demonstrate that the composite films/coatings can be prepared to have both a reasonably high conductivity and a good adhesiveness to silica glass and indium−tin oxide electrode (ITO). The enhancement of adhesion was evaluated by using the Scotch tape tests. The good adhesion and durability as well as electroactivity of the composite coatings were further established by cyclic

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(1) (a) Kanatzidis, M. G. *Chem. Eng. News* **1990**, *Dec 3*, 36. (b) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986, Vols. 1, 2.

(2) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(3) (a) Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth. Met.* **1990**, *36*, 139. (b) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317.

(4) (a) DeBerry, D. W. *J. Electrochem. Soc.* **1985**, *132*, 1027. (b) Elsenbaumer, R. L.; Lu, W. K.; Wessling, B. *Int. Conf. Synth. Met. Seoul, Korea*; Abstract No. APL(POL)1-2, 1994. (c) Wrobleski, D. A.; Benicewicz, B. C.; Thompson, K. G.; Bryan, C. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 265. (d) Wessling, B. *Adv. Mater.* **1994**, *6*, 226. (e) Wei, Y.; Wang, J.; Jia, X.; Yeh, J.-M.; Spellane, P. *Polym. Mater. Sci. Eng.*, in press. (f) Jasty, S.; Epstein, A. J. *Polym. Mater. Sci. Eng.*, in press.

(5) (a) Wei, Y.; Bakthavatchalam, R.; Whitecar, C. K. *Chem. Mater.* **1990**, *2*, 337. (b) Wei, Y.; Yang, D.; Tang, L.; Hutchins, M. K. *J. Mater. Res.* **1993**, *8*, 1143. (c) Wei, Y.; Yang, D.; Tang, L. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 273. (d) Wei, Y.; Wang, W.; Yeh, J.-M.; Wang, B.; Yang, D.; Murray, J. K. *Adv. Mater.* **1994**, *6*, 372. (e) Wei, Y.; Wang, W.; Yang, D.; Tang, L. *Chem. Mater.* **1994**, *6*, 1737.

(6) (a) Wei, Y.; Wang, W.; Yeh, J.-M.; Wang, B.; Yang, D.; Murray, J. K.; Jin, D.; Wei, G. *Am. Chem. Soc. Symp. Ser.*, in press. (b) Wei, Y.; Yang, D.; Bakthavatchalam, R. *Mater. Lett.* **1992**, *13*, 261.

(7) (a) Wei, Y.; Whitecar, C. K.; Yeh, J. M., results on the polyaniline−TEOS sol−gel composite materials to be published. (b) Whitecar, C. K. M.S. Dissertation, Drexel University, 1990.

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voltammetric studies. The effects of the material composition on the adhesion, conductivity, and mechanical properties were also investigated.

Experimental Section

Chemicals and Instrumentation. Aniline (Aldrich) was doubly distilled under a reduced pressure. Ammonium persulfate, $(NH_4)_2S_2O_8$ (99%, EM Science), was used as oxidant in the oxidative polymerization of aniline without further purification. Methyl methacrylate (MMA, Aldrich) and 3-(trimethoxysilyl)propyl methacrylate (MSMA, Aldrich) were distilled prior to the copolymerization. The free-radical initiator, benzoyl peroxide (Fisher), was purified by recrystallization from the methyl alcohol. Benzene (Fisher) and hexane (Fisher) were dried and purified by distillation following the standard procedures. (1*S*)-(+)-10-Camphorsulfonic acid (CSA, Aldrich), acetonitrile (Fisher), *m*-cresol (Aldrich), *N*-methyl-2-pyrrolidinone (NMP, Aldrich), and $LiClO_4$ (Johnson Matthey) were used as received without further purification. Electrical conductivity of the polymer films was measured using the standard four-probe technique. Electrochemical studies were performed on an EG&G PAR potentiostat/galvanostat (Model 173) with a universal programmer (Model 175). The Fourier-transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Thermogravimetric analysis and differential scanning calorimetry runs were taken on a DuPont 9900 thermal analysis system equipped with TGA 951 and DSC 910 modules in air or nitrogen at a programmed heating rate of 20 °C/min. Dynamic mechanical analysis was performed on the same system with DMA 983 module at a heating rate of 5 °C/min under argon at a fixed frequency of 1 Hz. The sample size for the DMA measurements was typically $0.6 \times 12.0 \times 0.1$ mm.

Synthesis of Polyaniline. Polyaniline in the hydrochloride salt form was prepared by chemical oxidation of aniline with ammonium persulfate as oxidant in 1 M HCl aqueous solution following the literature procedures.[8] The emeraldine base form of polyaniline (EB) was obtained by treating the salt form with 0.1 M NH_4OH. As a typical procedure, aniline (20.0 g, 214 mmol) was dissolved in 600 mL of 1 M HCl(aq) and the resultant solution was cooled to below 5 °C in an ice bath. A solution (400 mL) of 12.2 g (53.4 mmol) $(NH_4)_2S_2O_8$ in 1 M HCl was then added dropwise over 15 min with vigorous stirring. After ~1.5 h, the precipitate was collected on a Buchner funnel and was washed with a large amount of 1 M HCl until the filtrate became colorless. Upon drying under dynamic vacuum at room temperature for 48 h, the HCl-doped polyaniline was obtained as a green powder. Part of the polyaniline in the HCl salt form as synthesized above was converted into the base form by stirring ~3 g of the polymer powder in an excess amount (500 mL) of 0.1 M NH_4OH at room temperature for 3 h. Upon filtering and drying under dynamic vacuum for 48 h, the emeraldine base form of polyaniline was obtained as a blue powder.

Synthesis of the Sol–Gel Precursor. The synthesis and characterization of the sol–gel precursor, poly[methyl methacrylate-*co*-3-(trimethoxysilyl)propyl methacrylate] [P(MMA-MSMA)] were carried out following the previously reported procedures.[6] A representative procedure for the preparation of the copolymer P(MMA-MSMA) containing 80% MMA and 20% MSMA units is given as follows: 12.67 g (51.12 mmol) of 3-(trimethoxysilyl)propyl methacrylate, 20.44 g (204 mmol) of methyl methacrylate, 2.48 g (10.2 mmol) of benzoyl peroxide, and 64 mL of benzene were placed in a 250-mL three-neck round-bottom flask connected with a condenser, a thermometer, and a nitrogen gas inlet/outlet. Nitrogen gas was bubbled into the flask throughout the reaction. Under the magnetic stirring the solution was heated to 70 °C and maintained at that temperature for 3 h. The reaction mixture was then poured into about 800 mL of hexane to precipitate the copolymer. After filtration, the copolymer was dissolved in 50 mL of benzene followed by reprecipitating in 800 mL of hexane. This purification procedure was repeated twice. The purified copolymer was dried under vacuum at room temperature for 48 h. Copolymer P(MMA-MSMA) (20.0 g) was obtained in 60% yield. It is noteworthy that storage of the copolymer for a long time would result in a reduced solubility because of the interchain cross-linking reactions between the $-Si(OMe)_3$ groups.

Preparation of Polyaniline–P(MMA-MSMA) Sol–Gel Composite Films. As a typical procedure, 0.040 g (0.43 mmol based on the repeating ring-nitrogen unit) of polyaniline (EB) powder and 0.051 g (0.22 mmol) of camphorsulfonic acid powder were ground together in a mortar. This fine powder mixture was then slowly added to 4.0 mL of *m*-cresol with stirring under a fume hood to make ~1 wt % polyaniline solution, following a similar procedure in the literature.[9,10] To this solution, an appropriate amount of freshly prepared, finely ground P(MMA-MSMA) powder was added into the solution slowly with stirring in a period of 0.5 h to yield the sol–gel precursor-conducting polyaniline solution. The solution was diluted with a few drops of water and then cast onto a substrate (e.g., a microscope glass slide or an ITO electrode). The solvents and the small molecular products from the sol–gel reactions were allowed to evaporate under the hood for 48 h followed by drying under vacuum overnight to give crack-free and uniform P(MMA-MSMA)–polyaniline sol–gel composite coatings with various polyaniline contents as specified in the text. Caution should be taken in handling toxic *m*-cresol during the entire experiment.

Scotch Tape Test for the Adhesive Property. A simple Scotch tape test was employed to estimate the relative adhesiveness of the coatings to the substrate. The coating on the glass substrate (microscope slide from Fisher) was cut with a razor to make grid lines. The total test area was 4.0 cm^2 with each square dimension of 2×2 mm. Scotch tape (Scotch Magic tape with a width of 19.0 mm, by 3M) was applied firmly to cover the grid area at room temperature. After about 1 min, the tape was stripped off with one quick peeling. By counting the number of squares peeled off versus the total number of squares covered under the tape, the relative adhesiveness of the films of the polyaniline and of the polyaniline–P(MMA-MSMA) composite can be estimated. For each sample, at least three parallel tests were performed.

Cyclic Voltammetry. The cyclic potential sweeping technique was employed in this study. First, the polyaniline–P(MMA-MSMA) composite films were cast from the *m*-cresol solution of the CSA-doped polyaniline and P(MMA-MSMA) onto an indium–tin oxide (ITO) electrode followed by drying at room temperature 48 h under a fume hood. A typical film on the ITO had a dimension of 0.0136 mm in thickness, 8.11 mm in width, and 2.80 cm in length. All the cyclic potential sweeping experiments were performed in a single-compartment three-electrode quartz cell. The working electrode was the ITO electrode coated with the polyaniline–P(MMA-MSMA) composite films, the counter electrode was a platinum foil (area 3.0 cm^2), and the reference electrode was a saturated calomel electrode (SCE). The potential was cycled continuously between −0.4 and +0.6 V vs SCE at a scan rate of 50 mV/s in 100 mL of electrolyte solution consisting of 0.1 M $LiClO_4$ in CH_3CN. The effects of the amount of P(MMA-MSMA) in the films on the reversibility of electrochemical behavior and on the adhesion of the films during the potential cycling were investigated in the absence and in the presence of UV light. The UV source was a 15 W UV lamp (George W. Gates Co.) comprising mainly 365 nm wavelength. The distance between the light source and the surface of the electrolyte was 20 cm.

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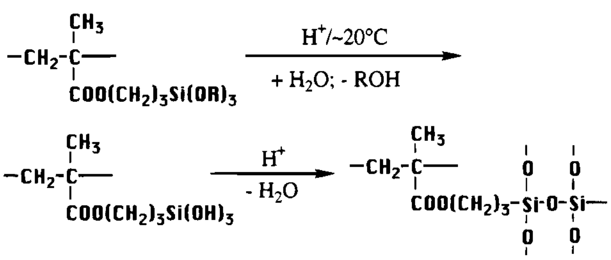
[8] (a) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcacer, L., Ed.; Reidel: Dordrecht, Holland, 1987. (b) Wei, Y.; Hsueh, K. F.; Jang, G.-W. *Macromolecules* **1994**, *27*, 518.

[9] (a) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91. (b) Cao, Y.; Smith, P. *Polymer* **1993**, *34*, 3139. (c) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *55–57*, 3514.

[10] Xia, Y.; MacDiarmid, A. G.; Epstein, A. J. *Macromolecules* **1994**, *27*, 7212.

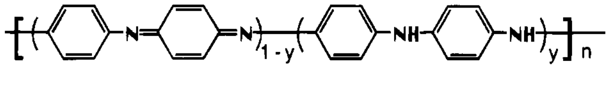
Scheme 1[a]



[a] R = CH_3.

Results and Discussion

The base forms of polyaniline can be described by a series of polymers that have different oxidation states as schematically represented by the following general formula



where the y value ranges from 0 for the fully oxidized polymer (so-called pernigraniline), to 0.5 for the half-oxidized polymer (emeraldine) and to 1 for the fully reduced polymer (leucoemeraldine).[3,8] High electrical conductivity (e.g., ~10 S/cm) can be usually obtained by doping the emeraldine base (EB) with a protonic acid (e.g., HCl). To prepare the polyaniline–P(MMA-MSMA) sol–gel composite materials, the sol–gel precursor P(MMA-MSMA) was added to a solution of EB and camphorsulfonic acid in *m*-cresol to afford an apparently homogeneous solution. Films were cast from this solution. During the dissolution and film formation, the sol–gel reactions (i.e., hydrolysis and polycondensation[11]) of the trialkoxysilyl functional groups in the P(MMA-MSMA) component proceeded under the acid (i.e., camphorsulfonic acid) catalysis as depicted in Scheme 1. Upon gelation (i.e., cross-linking) and drying, the polyacrylate–silica hybrid network was obtained and the polyaniline chains were trapped uniformly in the network. A cartoon presentation of this semiinterpenetrating type of three-dimensional network is given in Figure 1.

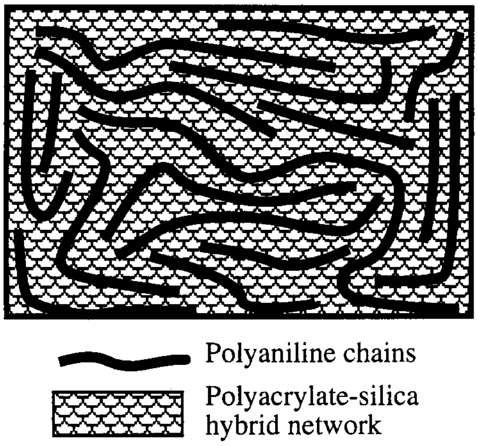


Figure 1. Cartoon presentation of the semiinterpenetrating type of three-dimensional network for the new composites of polyaniline with polyacrylate–silica hybrid sol–gel materials. At high loading levels, the polyaniline chains may overlap.

Table 1. Relations of the Composition of the Polyaniline (PANI)–P(MMA-MSMA) Sol–Gel Composite Films with the Conductivity at Room Temperature and with the Adhesion of the Films to a Silica Glass Substrate As Estimated from Scotch Tape Tests

compound code	feed composition (wt %) PANI	P(MMA-MSMA)	SiO_2 wt % in product calc[a]	found[b]	conductivity (S/cm)	Scotch tape test stripped area (%)[c]
CA	100	0	0	0	112.0	>90
CA1	90	10	1.7	2.2	16.9	30
CA2	80	20	3.5	3.1	6.1	3
CA3	70	30	5.2	6.5	3.4	1
CA4	50	50	8.6	11.2	2.5	<1
CA5	40	60	10.3	13.7	0.3	<1

[a] The SiO_2 contents (wt %) in the materials were calculated from the feed compositions with the assumption that all the $-Si(OMe)_3$ groups in P(MMA-MSMA) were completely converted to $-SiO_{1.5}$ after the sol–gel reactions. [b] The values were taken from the TGA curves at 700 °C. [c] The area percentage of the film was removed from the surface of the substrate.

The composite materials were light to dark green in color depending on the composition and film thickness. The composition of the polyaniline–P(MMA-MSMA) composite materials was varied from 0 to 60 wt % of P(MMA-MSMA) with respect to the polyaniline content as summarized in Table 1. The representative FTIR spectra of the composites, CSA-doped polyaniline and P(MMA-MSMA) are given in Figure 2. The stretching bands for the C=O groups in P(MMA-MSMA) appear at ~1732 cm^{-1} (Figure 2c). The bands around 1080 cm^{-1} are assigned to the Si–O stretching absorptions in P(MMA-MSMA).[5,6] The bands at 1510–1587 cm^{-1} are characteristic of the acid-doped polyaniline (Figure 2a).[9,12] In the spectrum of the composite (Figure 2b), these characteristic bands for both P(MMA-MSMA)- and CSA-doped polyaniline are present, though the intensity of the P(MMA-MSMA) bands is relatively low because of its low content (30 wt %) in the composite. This suggests that the structural integrity of both components has been largely retained during the composite-forming sol–gel process. Figure 3 shows typical TGA curves of the composite materials along with that of the CSA-doped polyaniline, as measured under an air atmosphere. In general, there appear to be several stages of weight loss beginning at ~180 °C and ending at ~650 °C, which might be correspondent to the evaporation of the CSA dopant followed by the structural decomposition of the polymers.[13] After 700 °C, the curves all become flat and mainly the inorganic residue (i.e., SiO_2) remains. From the amounts of the residue at 700 °C, the SiO_2 contents in the original composites can be obtained, which are reasonably comparable to

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(11) For leading references and reviews, see: (a) Schmidt, H.; Sieferling, B.; Philipp, G.; Deichmann, K. In *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; Wiley: New York, 1988; p 651. (b) Schmidt, H. *J. Non-Cryst. Solids* **1989**, *112*, 419. (c) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science, the Physics and Chemistry of Sol–Gel Processing*; Academic Press: San Diego, 1990. (d) Ulrich, D. R. *J. Non-Cryst. Solids* **1990**, *121*, 465. (e) Wilkes, G. L.; Huang, H.; Glaser, R. H. In *Silicon-Based Polymer Science (Adv. Chem. Ser. 224)*; Ziegler, J. M., Fearon, F. W., Eds.; American Chemical Society: Washington, DC, 1990; pp 207–226. (f) Calvert, P. *Nature* **1991**, *353*, 501. (g) Pope, E. J. A.; Asami, M.; Mackenzie, J. D. *J. Mater. Res.* **1989**, *4*, 1018. (h) Miller, T. M.; Brennan, A. B. *Polym. Mater. Sci. Eng.* **1994**, *70*, 276. (i) Novak, B. M. Adv. *Mater.* **1993**, *5*, 442. (j) Mackenzie, J. D. *Polym. Mater. Sci. Eng.* **1994**, *70*, 380.

(12) Tang, J.; Jing, X.; Wang B.; Wang, F. *Synth. Met.* **1988**, *24*, 231.

(13) Wei, Y.; Hsueh, K. F. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 4351.

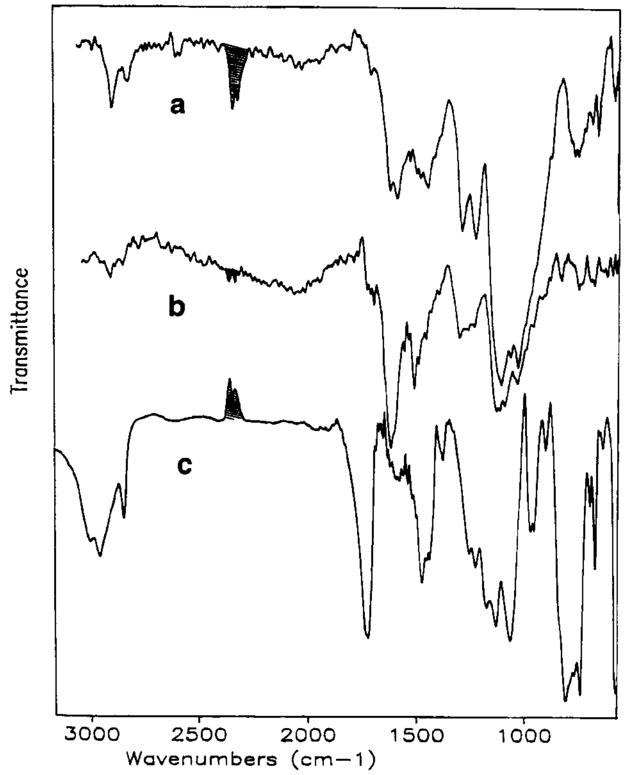

Figure 2. Infrared spectra of (a) camphorsulfonic acid-doped polyaniline, (b) the composite of polyaniline (70 wt %) with polyacrylate–silica hybrid sol–gel network, and (c) the precursor polymer, poly[methyl methacrylate-*co*-3-(trimethoxysilyl)-propyl methacrylate]. The shaded peaks were from background.

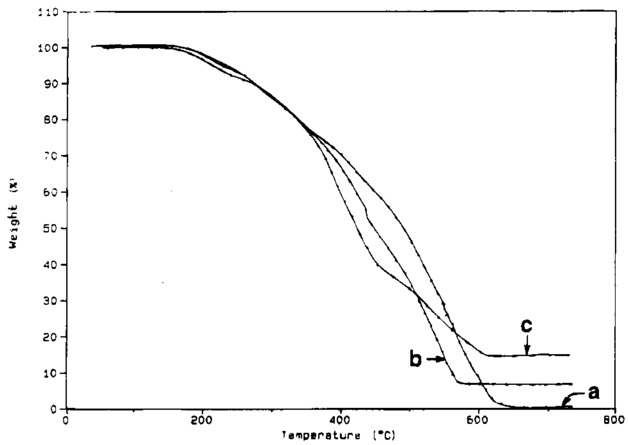

Figure 3. TGA curves of (a) camphorsulfonic acid-doped polyaniline, (b) the composite material containing 70 wt % of polyaniline, and (c) the composite containing 40 wt % of polyaniline.

the values calculated from the feed compositions (Table 1). The calculated SiO_2 contents tend to be lower than those determined from TGA probably because of incomplete decomposition of polyaniline in the silica matrix.

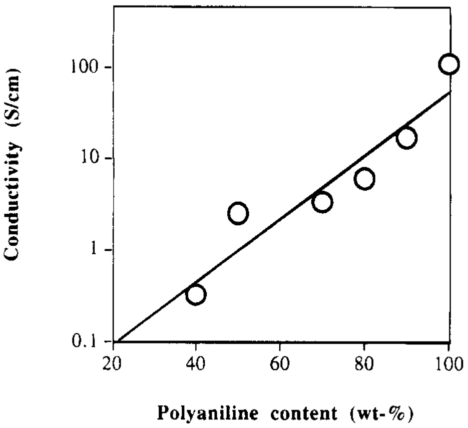

Figure 4. Plot of conductivity of the camphorsulfonic acid-doped polyaniline–P(MMA-MSMA) sol–gel composite films cast from the *m*-cresol solution against the wt % content of polyaniline in the films.

We have found that the bulk conductivity of the polyaniline–P(MMA-MSMA) sol–gel composite materials decreases as the amount of P(MMA-MSMA) is increased as shown in Figure 4. This is expected because the P(MMA-MSMA) component is not electrically conductive and only the polyaniline component contributes to the observed conductivity. Camphorsulfonic acid is a protonic acid. It has three functions in the system: (1) as a dopant to dope polyaniline to high conductivities, (2) to render the resulting doped polyaniline soluble in organic solvents,[9] and (3) as an acid catalyst for the sol–gel reactions of the precursor polymer P(MMA-MSMA).[5,6] As a control experiment, the EB alone was dissolved in NMP and the resultant solution was cast onto the silica glass slide followed by doping with aqueous 1 M HCl for 72 h. Such a prepared EB-HCl film showed a conductivity of about 2 S/cm. The camphorsulfonic acid-doped polyaniline with *m*-cresol as the film-casting solvent had a much higher conductivity. As shown in Table 1, the conductivity of the film without any P(MMA-MSMA) was 112 S/cm. The higher conductivity in the presence of *m*-cresol can be explained according to the so-called secondary doping concept.[10,14] Thus, *m*-cresol (as so-called secondary dopant) promotes the polyaniline molecular conformational change from a more "coillike" form toward a more "rodlike" (or more expanded coil) form. Since the rod conformation is more likely to have a longer conjugation length than the coil conformation, the attainment of the more rodlike conformation in the polyaniline would, therefore, enhance the bulk conductivity.[10,14] The employment of this system with higher conductivity than that of HCl-doped polyaniline enables us to meet the first objective of this research project, i.e., achieving reasonably high conductivities for the composite materials.

On the other hand, another objective is to increase the adhesive property of the conductive materials. By adding the precursor P(MMA-MSMA) into the system followed by the sol–gel reactions, the adhesion of the composite films was found to increase significantly. We evaluated the enhancement of adhesive property by two methods: the Scotch tape test and the durability of the films in cyclic voltammetric studies. The results of the Scotch tape test are given in Table 1. In general, the adhesion of the composite film to the silica glass substrate is much higher than the polyaniline film alone as evidenced by the smaller stripped areas. The adhesion is also increased as the amount of the P(MMA-MSMA) component is increased in the composites. It is particularly noteworthy that only a relatively small amount of the P(MMA-MSMA) content was sufficient to enhance the adhesiveness significantly. For the

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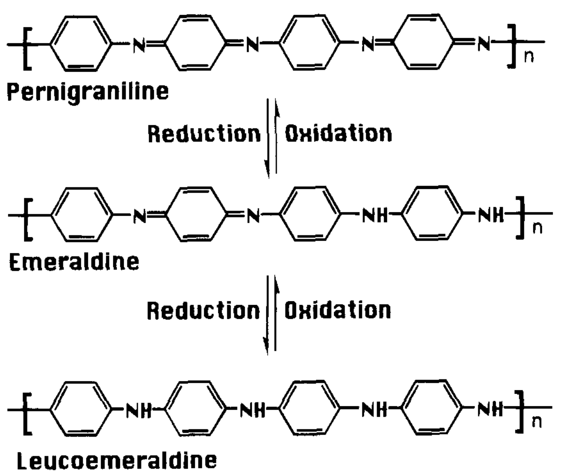
(14) (a) Min, Y.-G.; MacDiarmid, A. G.; Epstein, A. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 231. (b) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.*, in press.

Scheme 2



polyaniline film without P(MMA-MSMA), about 90% of the area under the Scotch tape was peeled off. This percentage was reduced to about 30% when the film was a composite material containing only 10% of P(MMA-MSMA). As the P(MMA-MSMA) content was increased to 30%, the film was almost intact when the tape was stripped off. The enhancement of the adhesion of the composite materials to the inorganic substrate is attributed to the sol–gel reactions of the P(MMA-MSMA) component in terms of two possible effects. First, the inorganic silica network as resulted from the sol–gel reactions has better thermodynamic compatibility with the inorganic glass substrate. Second, it is possible that the functional groups (i.e., –OH, etc.) on the substrate (e.g., silica glass) surface also react with the silanol functional groups (i.e., SiOH) in the P(MMA-MSMA) during the polycondensation process to form covalent bonding between the composite film and the substrate. It is important to note that the polyaniline–P(MMA-MSMA) composite film containing 30% of P(MMA-MSMA) still has a reasonably high conductivity of 3.4 S/cm. At this composition, both of our objectivities are achieved, i.e., the films have both good adhesion and conductivity at the same time.

The enhancement of the adhesion was further demonstrated by electrochemical test in a similar setting of which an electrochromic device can be fabricated. For these experiments, the polyaniline–P(MMA-MSMA) composite films were cast onto the ITO electrodes from the camphorsulfonic acid and *m*-cresol solutions. The composition of the films was varied to contain 0, 10, 20, or 30 wt % of P(MMA-MSMA). The coated ITO electrode was used as the working electrode in 0.1 M $LiClO_4$–CH_3CN electrolyte. The applied potential was cycled between –0.4 and +0.6 V vs SCE at a scan rate of 50 mV/s. At the higher applied potentials, the polyaniline is oxidized toward the formation of pernigraniline while at the lower potentials it is reduced toward the formation of leucoemeraldine as illustrated in Scheme 2.

During the potential cycling, the film color changes from the light yellowish green at low potentials to dark blue at high potentials as the redox reactions of polyaniline proceed.[3] In the absence of the P(MMA-MSMA) component, the polyaniline film became detached from the electrode surface after potential cycling for less than 1 day (~1800 cycles; note: completion of each cycle takes 48 s). There was only a small portion of the film (<10% of the original area) stuck on the electrode. The detached portion of the film was dark blue regardless of the applied potentials. In a striking contrast, the polyaniline–P(MMA-MSMA) composite films have drastically improved adhesion to the electrode under the same potential cycling process. For example, most (>80%) of the composite film containing 20 wt % of P(MMA-MSMA) adhered firmly to the ITO electrode after the potential cycling for at least three days (~5400 cycles). The small spotlike areas (<20%) of the film did not stick firmly to the ITO electrode surface and maintained a dark blue color during the potential cycling. These areas appeared to undergo a swelling–unswelling process as the potential was cycled. This phenomenon is not fully understood yet. It seems to be associated with some type of reversible gas generation/absorption. However, the film neither broke nor fell off from the electrode during the entire testing period. The results are even more remarkable when the composite films with higher P(MMA-MSMA) contents were employed. For example, the composite film containing 30 wt % of P(MMA-MSMA) (i.e., CA3) showed fully repeatable electrochemical behavior and full adhesion to the electrode after the potential cycling for at least 2 weeks (~25 200 cycles). The same experiments with the composite films were also carried out with exposing the films to UV radiation to evaluate the photochemical and electrochemical stabilities of the electroactive composite materials. No noticeable difference in the electrochemical behavior and adhesion was observed in comparison to the experiments in the absence of the UV radiation.

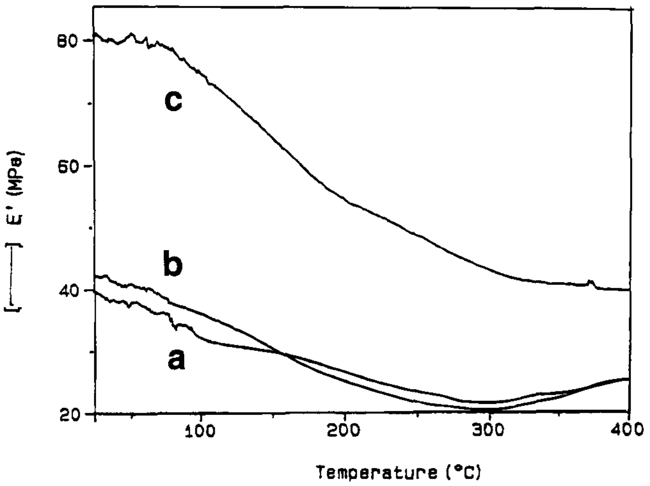


Figure 5. Relationship between the storage modulus (*E'*) and temperature as obtained from DMA measurements on the films of (a) camphorsulfonic acid-doped polyaniline, (b) the composite material containing 90 wt % of polyaniline, and (c) the composite containing 20 wt % of polyaniline.

The mechanical strength as represented by the modulus of the composite films was also found to be greater than that of the CSA-doped polyaniline. Figure 5 shows some typical dynamic mechanical analysis plots. In general, there is a major decrease in the storage modulus (*E'*) beginning at about 100 °C, which might be associated with the glass transition of polyaniline.[15] DSC curves also show correspondent endothermic baseline changes at the similar temperatures (~90 to ~140

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[15] Wei, Y.; Jang, G.-W.; Hsueh, K. F.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Polymer* **1992**, *33*, 314.

°C). The moduli for all the composite films (Figure 5b,c) at room temperature were higher than that for the CSA-doped polyaniline film (Figure 5a). Moreover, the greater the P(MMA-MSMA) content, the higher the modulus. This is a typical behavior of organic–inorganic composite materials. As the content of inorganic filler (i.e., SiO_2 wt % in this system) increases, the modulus of the composites becomes higher.

In summary, we have successfully prepared a new series of adhesive and conductive composite materials via the sol–gel reactions of the trialkoxysilyl groups in poly[methyl methacrylate-*co*-3-(trimethoxysilyl)propyl methacrylate] in the presence of camphorsulfonic acid-doped polyaniline in *m*-cresol solution. The composition of these composites can be varied by changing the stoichiometry of the starting materials. An increase in the content of the electronically conducting polyaniline in the composites results in a higher conductivity. As coatings, a higher content of the sol–gel precursor polymer leads to a greater enhancement of adhesion of the composite films to the inorganic silica glass and ITO electrode. The materials can be tailored to have an excellent adhesion to the substrates and a reasonably high electronic conductivity (e.g., 3.4 S/cm at the polyaniline content of ~70 wt %). We have also demonstrated that the new materials as coatings on the ITO electrodes under repeated potential cycling have much superior adhesion and durability over the conventional conducting polyaniline coatings. The mechanical strength as indicated by the modulus of the composite films was found to be higher than that of the polyaniline film. Further investigation is in progress in our laboratories to optimize the physicochemical properties of the composites and to explore their applications in fabrication of electronic, optical, and sensor devices.

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