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Synthesis of Hybrid Polyaniline/Carbon Nanotubes Nanocomposites in Toluene by Dynamic Interfacial Inverse Emulsion Polymerization Under Sonication

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ABSTRACT: This work describes an empirical study of *in situ* interfacial dynamic inverse emulsion polymerization process under sonication of aniline in the presence of nine different types of carbon nanotubes (CNT) in toluene. The polymerization method described in this work is simple and very fast (5 min) compared to the other literature reports (3–12 h). During polymerization, CNT are coated with polyaniline (PANI) forming a core-shell structure of nanowires as evidenced by transmission electron microscopy (TEM) and high-resolution scanning microscopy (HRSEM). HRSEM images and surface resistivity imply that PANI coating of CNT leads to a remarkable improvement in separation and dispersion of CNT in toluene, which otherwise would have rapidly coagulate and settle. Two of the nine different CNT studied have shown the lowest surface resistivities. Films of uniform thickness were successfully produced (HRSEM of cross-sections). The effect of film thickness on conductivity and optical properties is reported in the work. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polymeric nanocomposites are a new class of materials in which inorganic nanoscale particulates [e.g., clay, silica, carbon nanotubes (CNT)] are finely dispersed within an organic polymer matrix.[1–3] Homogeneous dispersions of nanoparticles in polymers using conventional processing techniques are difficult to produce, because nanoparticles tend to agglomerate. CNT were first reported by Iijima.[1] Since then, many studies have been reported regarding their manufacture, structure, and properties. CNT possess a remarkable combination of properties, that is, high strength and stiffness along with flexibility accompanied with high electrical and thermal conductivity, thus offering opportunities for the development of new nanocomposites.[2] Because CNT have poor "solubility" in most solvents and poor compatibility with polymeric matrices, fine dispersions are difficult to achieve. Moreover, CNT tend to agglomerate that lead to the loss of the intrinsic properties of a single CNT. There are several approaches to overcome agglomeration of the nanotubes: (i) using surfactants that adsorb on the CNT surface helping in their separation and dispersion; (ii) applying ultrasonic energy; (iii) functionalizing of CNT by chemical reactions with strong acids, silanes, etc.; (iv) *in situ* polymerization of monomers in the presence of CNT; (v) combination of these approaches.[3–8] Many reports appear in the literature regarding CNT, polymerization of aniline, preparation of polyaniline (PANI)/CNT nanocomposites, and various applications including thin, transparent, and conductive films.

Emulsion polymerization is a process where radical chain polymerization in oil in water systems comprising water, monomers, and surfactants occurs. The monomers polymerize within micelles and form stable colloidal dispersions, that is, emulsions.[9] Emulsion polymerization can also be carried out by an inverse water in oil emulsion polymerization procedure. Here, the continuous phase is the organic phase containing the monomer, while the aqueous solution containing the surfactant and initiator is emulsified by the surfactant. Inverse emulsion polymerization can be used for various monomers, including aniline.

Soares et al.[10] describe three methods to obtain dodecylbenzenesulfonic acid (DBSA)-doped PANI: (a) polymerization of aniline in acidic aqueous media followed by dedoping with ammonium hydroxide and redoping with DBSA, (b) an inverted emulsion polymerization method of aniline in toluene, and (c) *in situ* polymerization of aniline in the presence of DBSA in aqueous media. The reactions were conducted for 3–6 h. The PANI

Table I. Studied Nanotubes

	Type	Diameter (nm)	Length (μm)	Carbon purity (%)	Surface area (m²/g)	Company	Comments
N-7000	MWNT	9.5	1.5	90	250–300	Nanocyl, Belgium	
N-1000	SWNT	2	Several	>70	>1000	Nanocyl, Belgium	
N-1101	SWNT	2	Several	>70	>1000	Nanocyl, Belgium	>5% —COOH
N-2100	DWNT	3.5	1–10	>90	>500	Nanocyl, Belgium	
N-2101	DWNT	3.5	1–10	>90	>500	Nanocyl, Belgium	<1% —COOH
N-3100	Thin MWNT	9.5	1.5	>95	n/a	Nanocyl, Belgium	
Aligned MWNT	Aligned MWNT	10–20	5–15	>95	40–300	NanoAmor, USA	
Highly conductive MWNT	MWNT	50–100	5–10	>95	n/a	NanoAmor, USA	
Baytubes C 70 P	MWNT	13–16	1->10	>95	n/a	Bayer, Germany	

prepared by such different methods showed different structures: a uniform structure for *in situ* prepared PANI, a broad distribution for the redoped PANI, and a two-phase structure obtained by the inverse emulsion polymerization methods.

Huang et al.[11–13] reported the mechanism of interfacial aniline polymerization in an aqueous/organic biphasic system. In their work, aniline was dissolved in an organic solvent, and the aqueous phase contained the oxidant ammonium peroxydisulfate (APS) and a doping acid. The reactions were typically 12 h in duration and produced PANI nanofibers; unlike traditional oxidative polymerization that yields granular PANI. The resulting PANI particles' shape and size were not affected by the different solvents used (hexane, benzene, toluene, xylene, diethylether, carbon disulfide, carbon tetrachloride, chloroform, etc.).

PANI is one of the most studied conducting polymers due to its simple preparation, high conductivity, and environmental stability.[14] Many production methods of PANI are reported in the literature, as described by MacDiarmid[15]: "there are as many different types of PANI as there are people synthesizing it." PANI can be produced in organic or aqueous phases, using agitation or sonication, static interfacial, emulsion, and inverse emulsion polymerization methods. A water/oil microemulsion system has been successfully used for preparing PANI/MWCNT nanocomposites.[16] PANI has coated the MWCNT to form nanocables with a core-shell structure. The presence of MWCNT did not damage the backbone structure of PANI, and the conductivities exhibited by the PANI/MWCNT nanocomposites were higher than that of pure PANI.

Philip et al.[17] reported a route for producing PANI/MWCNT nanotubular composites. MWCNT were oxidized using potassium permanganate and then subjected to certain procedures to form *p*-phenylenediamine-functionalized MWCNT. Subsequently, polymerization of aniline took place in the presence of *p*-phenylenediamine-functionalized MWCNT. The resulting materials exhibited a uniform coating of PANI on the MWCNT.

A different technique was used by Ginic-Markovic et al.,[2] who used ultrasonically initiated, *in situ* emulsion polymerization to produce MWCNT/PANI nanocomposites. *In situ* polymerization allows the monomer to site-selectively interact with the CNT surface, producing an enclosed nanotube wrapped and stabilized by polymer. In comparison with pure PANI, the multiwalled CNT (MWNT)/PANI nanocomposites showed enhanced electrical conductivity and thermal stability. Konyushenko et al.,[18] Guo and Li,[19] and Zhang et al.[20] described the production of PANI-coated MWNT via an *in situ* polymerization method. There are several methods for the production of PANI, one of which presented by Soares et al.[10] describes an inverted emulsion polymerization method of aniline in toluene.

Hybrid PANI/CNT nanocomposites were produced by dynamic interfacial inverse emulsion polymerization under sonication.[8,21] During polymerization, MWNT were coated with PANI forming a core-shell structure of nanowires. The PANI coating of MWNT leads to a remarkable improvement in separation and dispersion of MWNT in chloroform, which otherwise would have rapidly coagulate and settle.

In the present work, the new *in situ* inverse emulsion polymerization method under sonication of aniline in the presence of CNT is described.[8,21] The reaction duration is very fast, reaching 82% conversion within 5 min of sonication and additional 30 min without sonication,[21] resulting in PANI-coated CNT structures.

Typical material applications include commercial transparent films products, such as touch screens, photovoltaic cells, flexible displays, and more. Approximate requirements for such films are surface resistance of 500 Ω/□ and 80% transparency in the visible region (VLT).[22,23]

Small et al.[24] have reported the preparation of printable inkjet using a water dispersion of PANI and high-CNT loading (32% wt). The printed films exhibited ∼ 5 kΩ/□ surface resistivity with 68% light transmittance.

The objective of this work is to identify promising CNT grades for achieving thin films with high conductivity and transparency; thus, nine different grades of CNT were studied and their performance compared.

EXPERIMENTAL

Materials

Aniline monomer was used after purification (Aldrich, USA). (±)-Camphor-10-sulfonic acid (β) (CSA; Riedel de-Haën,
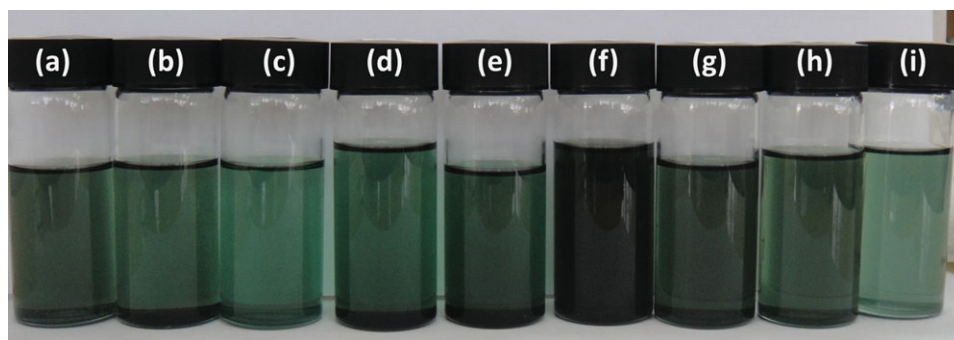
Figure 1. PANI/CNT dispersions in toluene of (a) N-7000, (b) N-1100, (c) N-1101, (d) N-2100, (e) N-2101, (f) N-3100, (g) Bayer (C70P), (h) aligned MWNT (NanoAmor), and (i) MWNT (NanoAmor). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sigma-Aldrich, Germany) and DBSA (Zohar, Israel) were used as received without further purification. Toluene (Bio Lab, Israel) was used as a solvent. Nine different nanotubes, shown in Table I, were studied: two types of single-walled, two types of double-walled, and five types of multi-walled CNT. APS was used as received (Riedel de-Haën, Sigma-Aldrich, Germany).

Preparation of Nanocomposites

The inverse emulsion polymerization procedure of aniline in organic solvent is conducted as previously reported[21]: a certain amount of dopant (CSA or DBSA) is dissolved in 20 mL toluene using magnetic stirring. Different concentrations of distilled aniline are added, and a clear solution is formed. Vibra cell VCX 750 (Sonics & Materials, USA) ultrasonic liquid processor was used to disperse the CNT and to accelerate the polymerization process. CNT are added *in situ*, before polymerization begins, to the toluene solution. CNT concentration is usually 0.05% wt of the dispersion. APS dissolved in 1-mL distilled water and is added to the solvent/aniline solution followed by sonication at 4°C for 5 min. The PANI/CNT dispersion then serves for film formation using a series of coating rods to produce films of different thicknesses (K Hand Coater Large Starter Set, RK Print Coat Instruments, UK). The thin films were washed with ethanol to remove the dopant excess and aniline residue. A reference sample without CNT was prepared using the same procedure. The molar ratios of aniline : dopant : APS are 1 : 0.5 : 0.25, 1 : 1 : 0.25, or 1 : 2 : 0.25, respectively.

Characterization

The PANI/CNT nanocomposite's morphology was studied using LEO 982 (Cambridge, UK) high-resolution scanning electron microscopy (HRSEM), equipped with a high-resolution field emission gun, operated at a 4 kV accelerating voltage at a 3–4-mm working distance, and an in-lens detector of secondary electrons. Samples were freeze-fractured and gold-sputtered before observation.

A two-point probe technique, according to ANSI/ESD STM 11.13[25]: two-point resistance measurement was used to measure the electrical surface conductivity of the films produced, thus resulting in surface resistivity Ohm/□ values.[26]

Light transparency and haze of the films were measured using Qualitest Haze-Gard Plus instrument (USA).

Transmission electron microscopy (TEM) micrographs were obtained for specimens prepared by spraying the dispersions using N_2 as carrier. Specimens were examined in a FEI T20 (FEI Company, USA) TEM operated at 200 kV with a LaB6 electron source and an FEI Supertwin Objective Lens. This microscope is also equipped with a plate camera and a 1 K × 1 K Gatan 694 retractable slow-scan CCD. Images were also obtained by FEI Titan 80–300 S\TEM (FEI Company) equipped with a monochromator for sub-eV energy resolution (80–300 kV), an aberration corrector for the objective system (80–300 kV), a high-resolution energy filter, and a high-resolution slow-scan CCD.

RESULTS AND DISCUSSION

Figure 1 demonstrates clear dispersions of PANI/CNT in toluene of (a) N-7000, (b) N-1100, (c) N-1101, (d) N-2100, (e) N-2101, (f) N-3100, (g) Bayer (C70P), (h) aligned MWNT (NanoAmor), and (i) MWNT (NanoAmor) prepared as previously described. The dispersions were stable for long periods of time without any visible precipitation. It was previously reported that our dynamic inverse emulsion polymerization under sonication has resulted in PANI.[21]

Figure 2 depicts high-resolution scanning electron micrographs of dry cross-sections produced by film fracturing normal to the film's plane, prepared from two wet films: (a) 6 and (b) 24 μm. The films were deposited from 0.2% wt N-7000 emulsion on silicon wafers using coating rods. The measured dry thicknesses for the 6 and 24 -μm wet films are ∼ 500 and 1600 nm, respectively. The CNT are well dispersed within the polymeric matrix. A desired dry thickness can be determined by a selected wet thickness and by the solid content. The solid content of the emulsion used for the preparation of the films is 12% wt. The thickness ratios of wet to dry films for the 6 and 24-μm wet films are 12 : 1 and 15 : 1, respectively.

Figure 3 depicts HRSEM images of PANI-coated DWNT, polymerized in toluene. The surface of the CNT has been coated with PANI, and it appears similar to the surface of neat PANI.[8,21] Similar images were obtained for all the SWNT and DWNT studied. The CNT/PANI tube average diameters are summarized in Table II, showing that the nanotubes were coated with PANI. Similar findings were described elsewhere,[2,18–20] where PANI has coated the CNT. The thickness of PANI coating is 16–34 nm. Some free PANI, unattached to the CNT surfaces, is accumulated on the wafer's surface (darker areas).
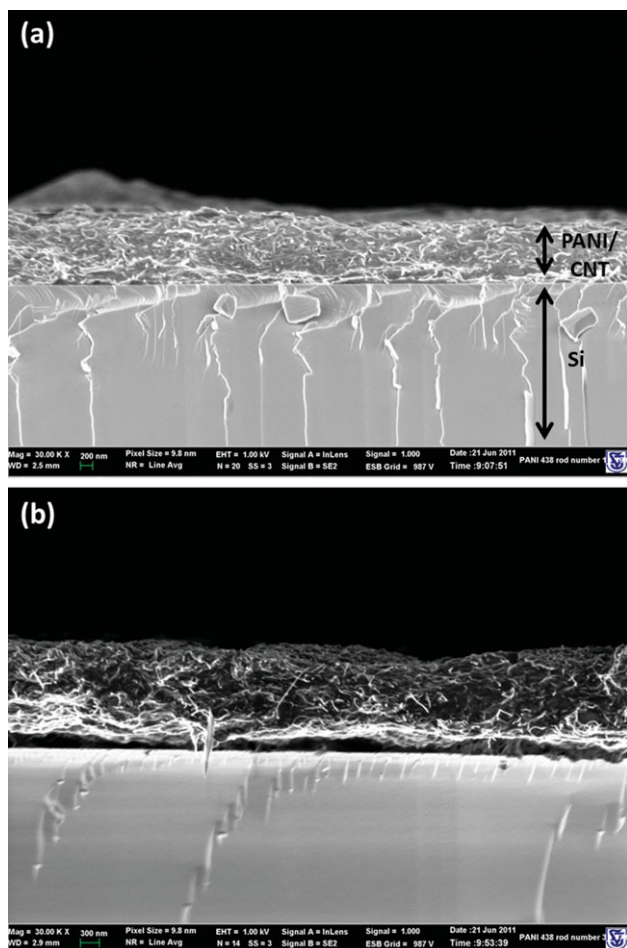
Figure 2. HRSEM of dry cross-section images (a) 6 μm and (b) 24 -μm wet-thickness films deposited from 0.2% wt N-7000 emulsion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 depicts HRSEM images of PANI Nanocyl 7000 MWNT, polymerized in toluene. Similar images were obtained for all the MWNT studied. The surface of the MWNTs has been changed, similar to the SWNT and DWNT. The CNT/PANI
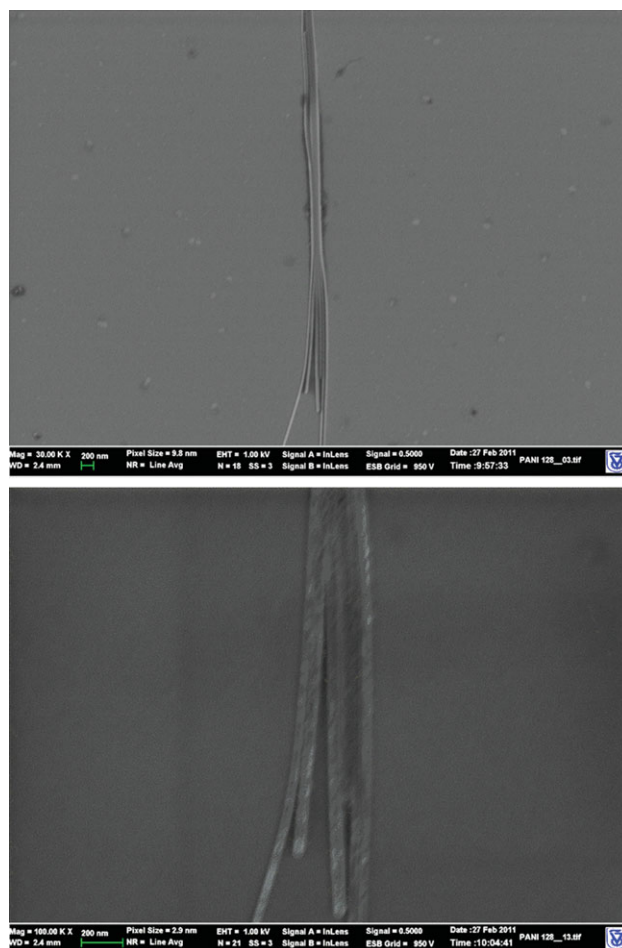
Figure 3. HRSEM images of PANI-coated DWNT, polymerized in toluene, two magnifications. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tube average diameters are summarized in Table II, showing that the nanotubes were coated with PANI. The thickness of PANI coating is 11–34 nm.

PANI has coated all the studied CNT, during polymerization, regardless of their surface characteristics. Aniline selectively

Table II. Coating Properties Summary of PANI-Coated Nanotubes

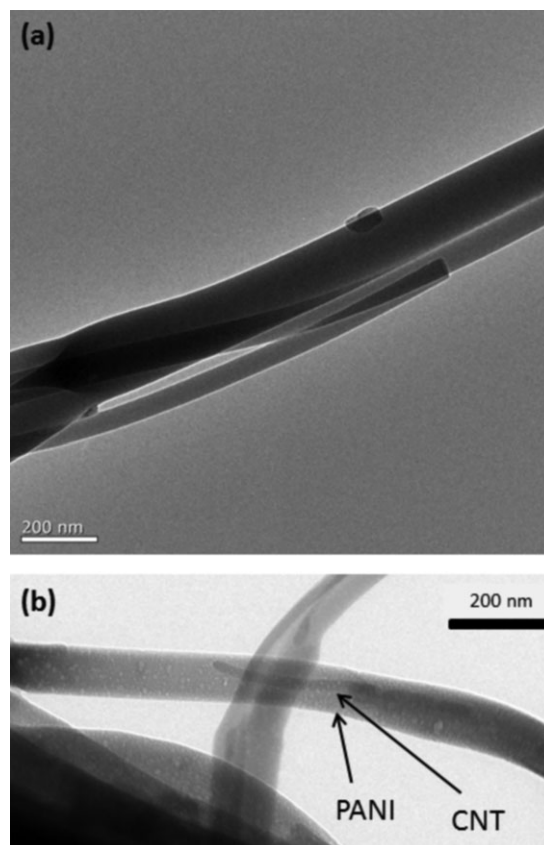|	Type	Neat CNT diameter (nm)	After polymerization diameter (nm)	Thickness of PANI coating (nm)	Resistivity (kΩ/□)	Comments
N-7000	MWNT	9.5	78	34.25	160	
N-1000	SWNT	2	34	16	150,000	
N-1101	SWNT	2	69	33.5	250,000	
N-2100	DWNT	3.5	42	19.25	500,000	
N-2101	DWNT	3.5	40	18.25	400,000	
N-3100	Thin MWNT	9.5	46	18.25	690	
Aligned MWNT	Aligned MWNT	10–20	33	11.5	700,000	Neat diameter of 10 nm
Highly conductive MWNT	MWNT	50–100	50	0	54,000	Neat diameter of 50 nm
Baytubes C 70 P	MWNT	13–16	71	29	500,000	Neat diameter of 13 nm

polymerizes upon the external surface of the nanotubes, whereas the DBSA molecules expose their aliphatic tails toward the solvent medium contributing to the successful dispersion of CNT. In the absence of PANI, CNT rapidly agglomerates and precipitates in the solvent.[8,21]

Figure 5 depicts TEM images of sprayed dispersions: (a) neat PANI and (b) PANI/CNT, polymerized in toluene. Figure 5(a) shows neat PANI fibers with diameters of 60–180 nm. These fibers were spontaneously created during dispersion spraying using N_2 flow. Figure 5(b) shows several PANI/CNT fibers, where nanotubes are embedded within the PANI fibers. The top fiber was intensely irradiated. Because only PANI decomposes when irradiated, it is possible to distinguish between PANI and CNT. The PANI fiber exhibits a diameter of ∼ 86 nm, whereas the nanotube diameter is ∼ 22 nm. This further confirms the suggested structure.[8]

Table II summarizes film resistivity of films deposited from the PANI/CNT dispersions with aniline : DBSA : APS molar ratios of 1 : 1 : 0.25 and 0.05% wt CNT. The wet-film thickness is 24 μm. Most of the CNTs have shown high-film resistivity levels. However, N-7000 and N-3100 MWNT exhibited relatively low resistivities of 160 and 690 kΩ/□, respectively. Thus, further

Figure 5. TEM images of sprayed dispersions: (a) neat PANI and (b) PANI/CNT.

characterization was continued using N-7000 and N-3100. The electrical volumetric conductivity for a PANI/N-7000 bulk sample was high: 2.4 S/cm. However, because the bulk thickness is at least four orders of magnitude higher than the film thickness, it is irrelevant for the current manuscript, and value surface resistivities are the relevant ones.
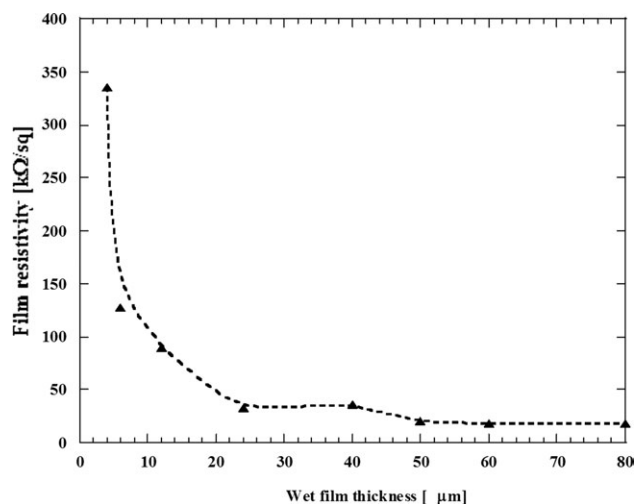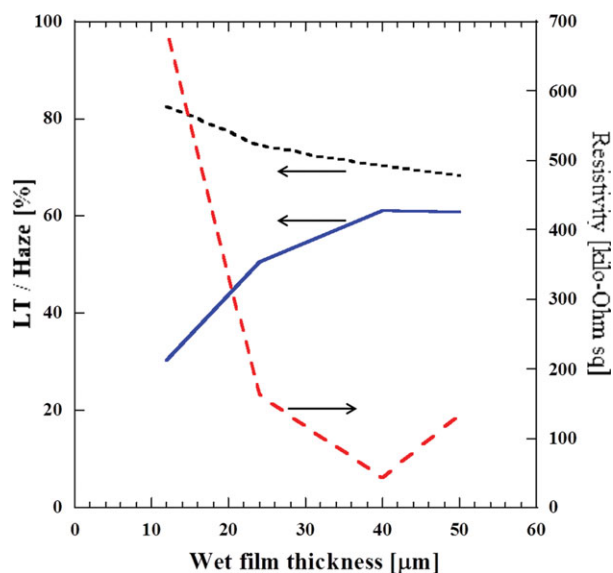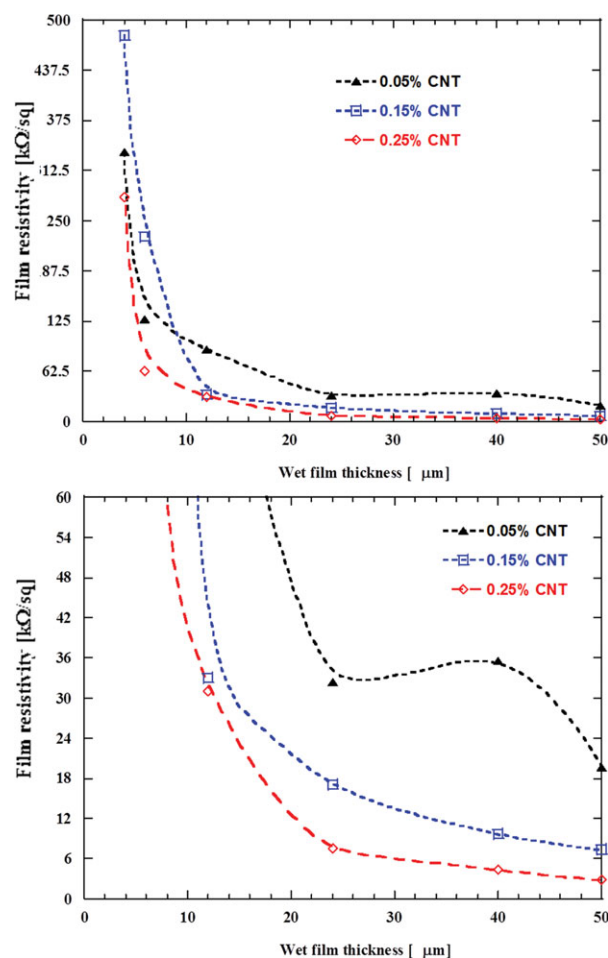

Figure 4. HRSEM images of PANI-coated Nanocyl 7000 MWNT, polymerized in toluene, two magnifications. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
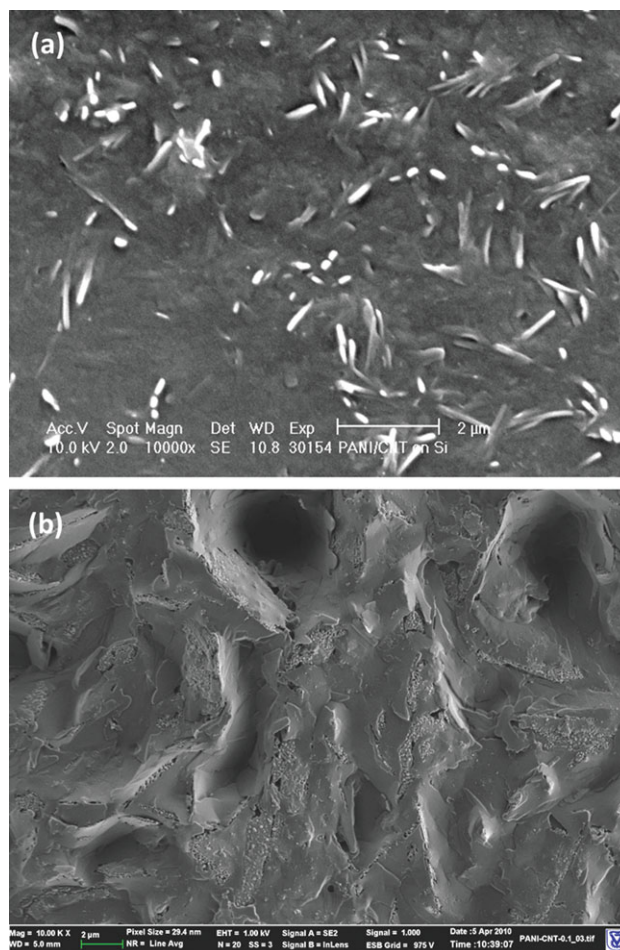

Figure 6. PANI/CNT film resistivity dependence on deposited wet-film thickness.

Figure 7. Film resistivity, light transparency, and haze dependence on deposited wet-film thickness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. Film resistivity dependence on deposited wet-film thickness and CNT concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. HRSEM images of dry films: (a) 0.05% wt N-7000 and (b) 0.5% wt N-7000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 depicts film-resistivity dependence on wet-film thickness. The films were fabricated using different coating rods resulting in various wet-film thicknesses. The films were deposited from PANI/CNT dispersions with molar ratios of aniline : DBSA : APS 1 : 1 : 0.25 and 0.05% wt N-7000 MWNTs. The film resistivity decreases from 335 kΩ/$\square$ for the thinnest film down to 18 kΩ/$\square$ for the thickest one. However, because the resistivity levels off at $\sim$ 24 -μm wet thickness, films for further investigation were 12–50 -μm thick. Alcohols improve the film's conductivity and optical properties dramatically and are currently under investigation.

Figure 7 depicts film resistivity, light transparency, and haze dependence on wet-film thickness. The films that were deposited from PANI/CNT dispersions with molar ratios of aniline : DBSA : APS are 1 : 1 : 0.25 and 0.05% wt N-3100 MWNTs, using the coating rods. Both film resistivity and light transparency decrease, while haze increases as the film thickness increases. Transparency is relatively high ($\sim$ 75%), resistivity values level off at $\sim$ 24 μm, and the films for further investigation were 12–50 μm thick.

Figure 8 depicts film-resistivity dependence upon wet-film thickness and CNT concentration. The films that were deposited

from PANI/CNT dispersions with molar ratios of aniline : DBSA : APS are 1 : 1 : 0.25 and 0.05, 0.15, and 0.25% wt N-7000 MWNTs, using the coating rods. All three compositions exhibited the same trend, where film resistivity decreases as thickness increases. The resistivity levels off at ∼ 24 μm for the 0.05% wt sample. The resistivity levels off at ∼ 12 μm for the 0.15 and 0.25% wt samples. The resistivity decreases as CNT concentration increases due to increasing pathways available for electric current conduction.

Figure 9 depicts HRSEM images of (a) 0.05% wt N-7000 and (b) 0.5% wt N-7000. Figure 9(a) shows good CNT dispersion within the PANI matrix. However, when the CNT concentration was increased by an order of magnitude to 0.5% wt [Figure 9(b)], agglomerates were formed. Although the increased CNT concentration has decreased the film resistivity, transparency has been dramatically decreased. Thus, CNT concentration should not exceed ∼ 0.25% wt for all the studied CNT grades to achieve a combination of balanced properties.

The technology described in this work and its principles have led the authors to remarkable achievements in relation to the performance of thin conductive, transparent films, particularly a low-surface resistivity (<1 kΩ/□) has been achieved. The combination of the resulting properties is unparalleled with the other literature reports. Solvent's posttreatment procedures of the dry films have added important improvements.

In summary, this work presents a study of parameters important for the production of conductive PANI/CNT thin films characterized by a combination of desired resistivity, transparency, and haze properties.

CONCLUSIONS

This work describes *in situ* dynamic interfacial inverse emulsion polymerization method of aniline conducted in the presence of different CNT types under sonication, resulting in PANI-coated nanotubes. The dispersions prepared were found stable for several months. The nanotubes are coated with PANI. PANI interacts with the nanotubes and thus exhibits improved film properties. Surface resistivity was found lowest for N-7000 and N-3100 MWNTs. The film resistivity and light transparency decrease while haze increases as the film thickness increases. The polymerization method described in this work is simple and very fast compared to the other literature reports. The technology described in the work has led to outstanding performance of thin films, particularly low-surface resistivity (<1 kΩ/□). The combination of the resulting properties is unparalleled with other literature reports. Solvent posttreatment procedures of the dry films have shown the significant further improvement.

ACKNOWLEDGMENTS

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