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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Wang, Xin , Wang, Xuyun , Lee, Joong-Hee and Kalappa, Prashantha(2006) 'Synergistic Enhancement on the Conductivity of Polyaniline via Copolymerization and Carbon Nanotubes', Journal of Macromolecular Science, Part A, 43: 9, 1477 – 1484

To link to this Article: DOI: 10.1080/10601320600820512

URL: <http://dx.doi.org/10.1080/10601320600820512>

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Synergistic Enhancement on the Conductivity of Polyaniline via Copolymerization and Carbon Nanotubes

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Polyaniline and aniline/5-aminoisophthalic acid (AIA) copolymer have been successfully synthesized via oxidation polymerization, as well as their composites containing carbon nanotubes. AIA can benefit the formation of quinoid rings in the aniline polymerization and promote the conductivity of the copolymer. IR and Raman spectra reveal AIA/aniline copolymers have both benzenoid and quinoid rings, as well as their doped structures. Good conductivity of the copolymer could be achieved at high AIA content. Carbon nanotubes can also simultaneously promote the formation of quinoid rings in the copolymer, enhance conductivity and improve thermal stability. The copolymerization of AIA with aniline and the introduction of carbon nanotubes show a synergistic enhancement of conductivity.

Keywords oxidation, carbon nanotubes, carbon composites, thermal conductivity

Introduction

Since its discovery in 1991 by Iijima (1), carbon nanotubes (CNT) have started a lasting and comprehensive investigation. The purification and chemical modification of carbon nanotubes have provided good adaptability for different kinds of applications. To take advantage of their excellent mechanical properties, carbon nanotubes have been introduced into polymeric matrix as fillers (2–6).

Carbon nanotubes have excellent electric conducting ability arising from its subtle structure. Other than imparting electrical properties to non-conducting materials, carbon nanotubes/conducting polymer composites have a promising future in electronic applications. Among the conducting polymers, polyaniline (PANI) is featured by its easy preparation by electric-chemical or chemical methods. PANI can be reversibly doped and de-doped, providing an easy way to control its conductivity by the degree of doping. Sun reported the high dissolution and strong light emission of carbon nanotubes

Received and Accepted April 2006.

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in aniline solvents (7). From the view of chemical structure, NT should be a good electron acceptor, while aniline is a fairly good electron donor. The donor-acceptor interaction between carbon nanotubes and PANI was confirmed in the composites prepared using *in situ* polymerization (8) or solution mixing (9). Wan (10) used sulfonated multi-walled carbon nanotubes as the protonic dopant and self-assembled template for the formation of PANI nanolines. Directed by cationic surfactant, Zhang (11) synthesized similar PANI/CNT nanolines. However, conductivities of the nanolines in both cases were unsatisfactory due to the low doping level.

Here, we present the synthesis and characterization of ternary PANI/5-aminoisophthalic acid (AIA)/CNT composites, which have better conducting behavior and thermal stability than binary composites of PANI/CNT and the pristine copolymer without CNT.

Experimental

Materials and Agents

Aniline ($d = 1.022$, MW = 93.13) and ammonium peroxydisulfate (APS), MW = 228.20, were purchased from Shinyo Pure Chemicals Co. LTD, Minoo OSAKA, Japan. 5-Aminoisophthalic acid (AIA), MW = 181.15, was obtained from Acros organics. AIA has a chemical structure similar to aniline, but with two extra carboxyls, used as monomer for copolymerization with aniline. Multi-walled carbon nanotubes (MWNT), manufactured by the CVD method, having a Grade >95vol%, was obtained from ILJIN Nanotech Co LTD, Korea.

Chemical Treatment and Synthesis

Oxidation of MWNT. A fixed amount of multi-walled carbon nanotubes were added into the mixture of concentrated nitric acid (60%) and concentrated sulfuric acid (97%) with a volume ratio 1/3, then refluxed at 80°C for 40 min. After thorough washing by de-ionized water and drying, the solid precipitate was rubbed with a mortar and pestle to obtain oxidized carbon nanotubes (o-CNT).

Oxidation Polymerization of Aniline and in-situ Polymerization with o-CNT. In a typical oxidation polymerization of aniline, 200 ml de-ionized water was first adjusted to PH 1.0 by concentrated hydrochloride acid. Aniline (12 ml) was added under an ice bath, and the system was kept stirring for 30 min. APS (22.6 g) was dissolved in 60 ml de-ionized water and added dropwise to the aqueous aniline solution. The polymerization system was kept for 24 h under an ice bath. The solid precipitates after washing and filtration is doped PANI.

In-situ polymerization of aniline with o-CNT is a similar process. Before the addition of tAPS, o-CNT was first sonicated in aniline solution for 40 min and then kept stirring for 60 min.

Copolymerization of Aniline and AIA and Preparation of Copolymer/CNT Composites

Aniline (20 ml) was first stirred in de-ionized water (PH = 1.0). AIA (1.988 g), dissolved in hydrochloride acid, was then poured into the aniline solution. A fixed amount of APS was added dropwise to start the 24 h copolymerization, which was maintained in an ice

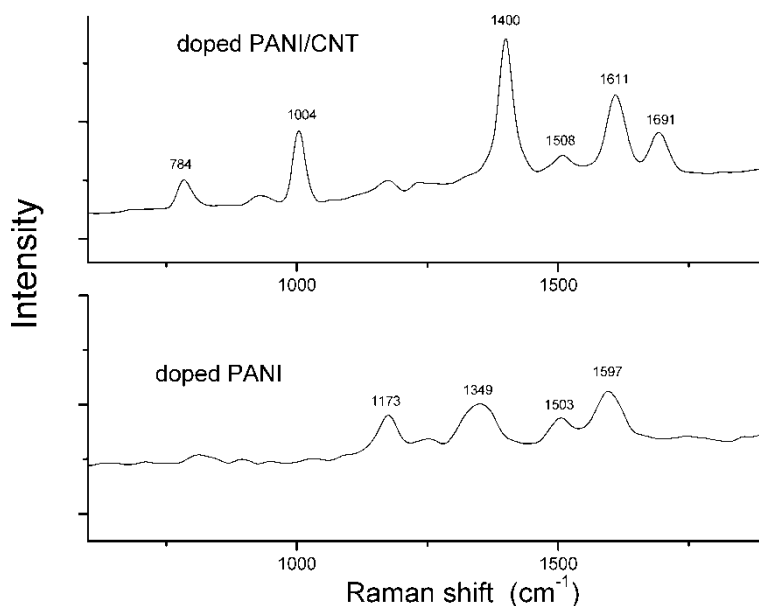


Figure 1. Raman spectra of doped PANI and PANI/CNT composite.

bath. The copolymer should have an approximate 10/0.5 molar ratio of aniline to AIA. If 3.976 g and 5.964 g of AIA were used to copolymerize with aniline, the molar ratio of the copolymer should be 10/1 and 10/1.5, respectively. In the *in-situ* copolymerization with o-CNT, o-CNT was first sonic dispersed in AIA solution and then stirred with aniline together before copolymerization started.

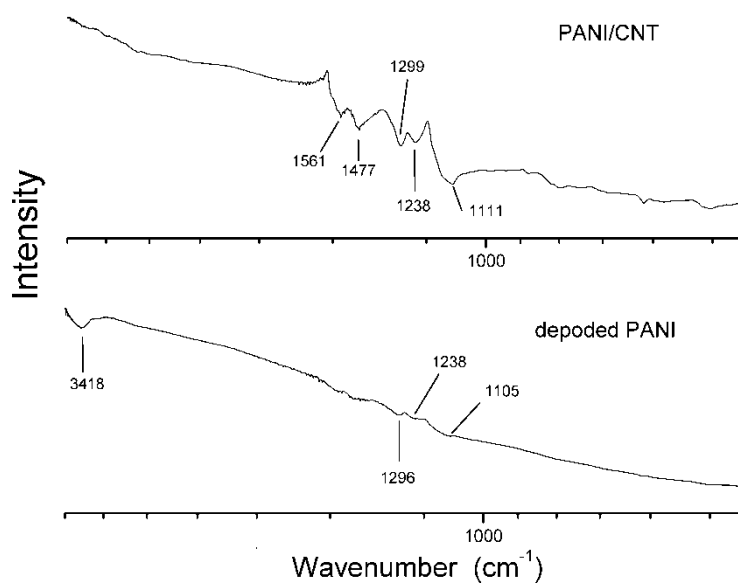


Figure 2. IR spectra of PANI and PANI/CNT composite.

Table 1
The resistance of PANI and PANI/CNT composites

Samples	Resistance (ohm/m ²)	Measure voltage (V)
De-doped PANI	$2.0\text{--}3.0 \times 10^8$	100
doped PANI	$1.4\text{--}1.9 \times 10^6$	10
PANI/CNT (5 wt%)	$8.0\text{--}10.0 \times 10^4$	10

Characterization

Resistance. The resistance of powder samples were measured at room temperature in a MCP-HT450 typed Resistivity Meter, Mitsubishi Chemical Corp., Tokyo, Japan. The voltage used was 10 or 100 V according to the magnitude of the resistance.

Raman Spectroscopy. The Raman spectrum was measured with a FT-Raman Spectrometer, RFS-100S type, Bruker Co. LTD, Germany.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR measurements were conducted on a Nicolet Impact 400 FTIR Spectrometer, using a thin film of sample powders and KBr.

Thermogravimetric Analysis (TGA). The thermal stability of conducting polymers and their composites were measured in a TGA cell, with a TA instrument rate of 20°C/min from 50 to 700°C under nitrogen flow.

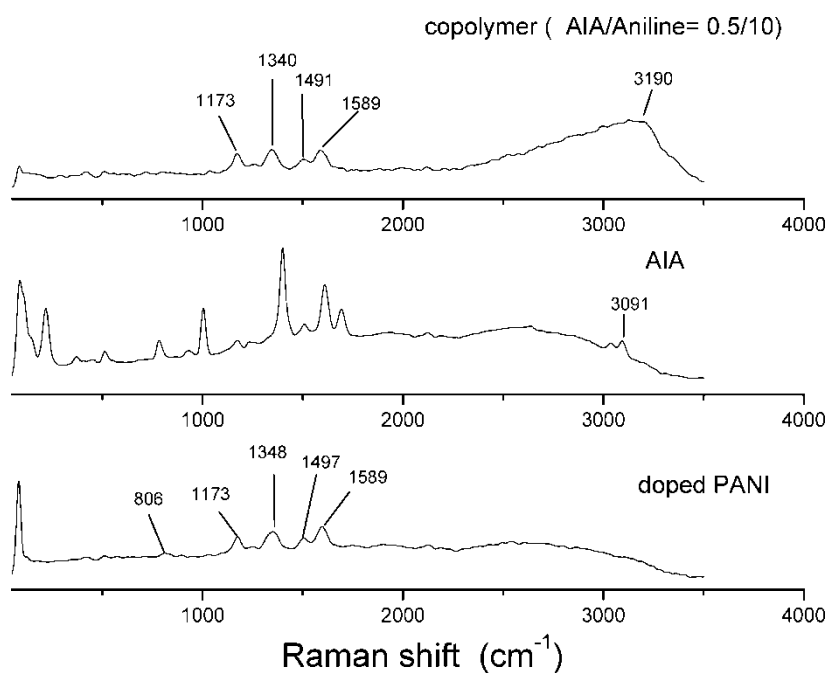


Figure 3. Raman spectra of PANI and AIA/aniline copolymer.

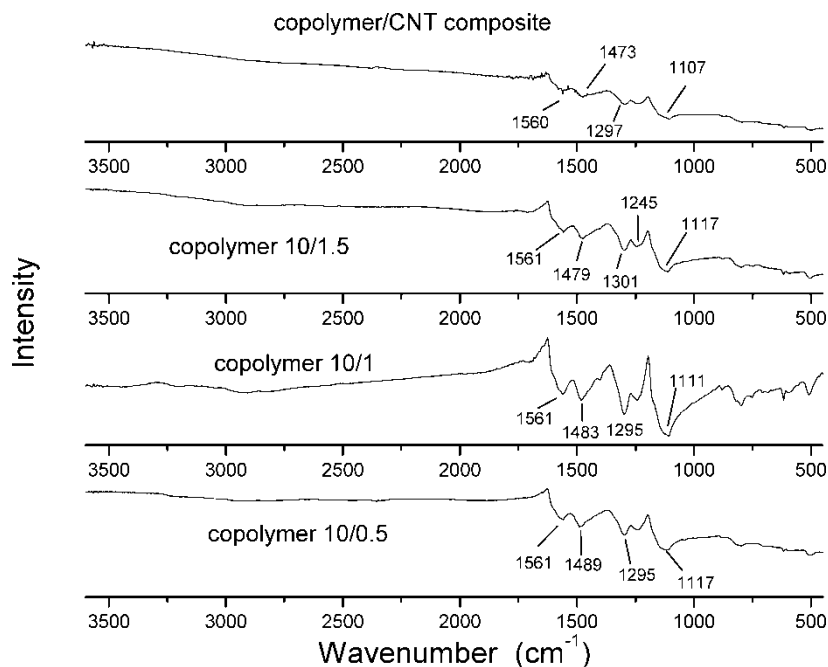


Figure 4. IR spectra of different copolymers and copolymer/CNT composite with aniline/AIA = 10/0.5 and 4 wt% CNT.

Results and Discussions

Spectrometric Behavior and Conducting Properties of PANI and PANI/CNT Composites

The doped structure of PANI, prepared by oxidation polymerization, can be identified from the Raman spectra shown in Figure 1. PANI doped by hydrochloride acid has an apparent absorption of C-N⁺ at 1349 cm⁻¹. Other peaks are the contributions of C-C stretching of the benzenoid ring at 1597 cm⁻¹, N-H bending at 1503 cm⁻¹ and C-H bending of the benzenoid/quinoid ring at 1173 cm⁻¹. PANI/CNT composite has a

Table 2
Resistance and relative IR absorption

Samples	Resistance (ohm/m ²)	Relative IR absorption		
		Electron-like carriers	Benzenoid ring	Quinoid ring
PANI/CNT	8.0–10.0 × 10 ⁴	1.67	1.14	1
Copolymer (10/0.5)	2–8 × 10 ⁶	1.98	1.20	1
Copolymer (10/1.0)	1.3–1.5 × 10 ⁴	1.77	1.13	1
Copolymer (10/1.5)	< 10 ⁴	1.84	1.12	1
Copolymer (10/0.5)/CNT	< 10 ⁴	1.41	1.05	1

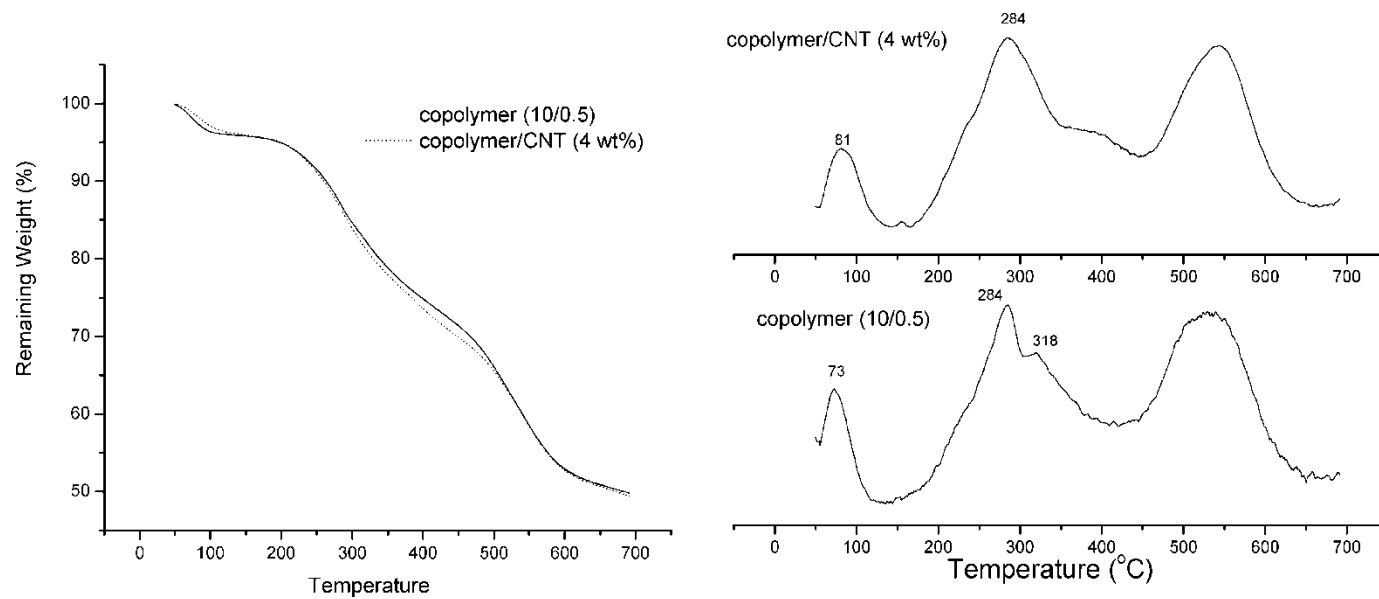


Figure 5. TGA curves of aniline/AIA copolymer and its composite.

similar absorption to PANI, excepting the strong absorption of free charge carriers at 1400 cm^{-1} . In addition, the peak at 784 cm^{-1} is the contribution of the deformation of a benzenoid ring.

The IR spectra of PANI/CNT composite in Figure 2 indicates the same free charge carriers, whose absorption peaks at 1111 , 1561 and 1477 cm^{-1} are the contribution of C-C stretching of quinoid and benzenoid rings, respectively. The 1299 cm^{-1} peak is the C-N bond contribution. The Raman and IR spectra confirm the much stronger free charge carries in PANI/CNT composite than the doped PANI. The resistance of PANI and its composites are shown in Table 1. As shown, the resistance decrease confirms the free charge carries in the PANI/CNT composites.

Spectrometric Behavior and Conducting Properties of AIA/Aniline Copolymer and Copolymer/CNT Composites

AIA/aniline copolymer has the same Raman shift as doped PANI, as shown in Figure 3, indicating their similar chemical structures. The IR spectra of the copolymers, with different molar ratio of aniline/AIA in Figure 4, are almost the same. The absorption around 1110 cm^{-1} is the contribution of electron-like carriers. The peak at 1561 and $1480\text{--}1490\text{ cm}^{-1}$ are the contribution of quinoid and benzenoid rings, respectively.

A quantitative analysis on the relative IR absorption of different chemical groups is shown in Table 2. The ratio of benzenoid ring's absorption to the quinoid ring decreases with the AIA composition in the copolymer, indicating AIA can induce the formation of quinoid rings in the oxidation polymerization. The resistance of the copolymers drop with the AIA content, though the ratio of electron-like carries' absorption to quinoid ring decreases.

The introduction of carbon nanotubes can strongly induce the formation of a quinoid ring. The ratio of quinoid ring's absorption to the benzenoid ring decreases from 1.20 to 1.05 when 4 wt% carbon nanotubes is added. Simultaneously, the composite exhibits a notably promoted conductivity, as shown in Table 2.

Both AIA and CNT will induce the formation of quinoid rings in the backbone of the conducting polymer and enhance its conductivity. Comparing the conductivity of PANI/CNT composite and copolymer/CNT composite, a synergistic enhancement of AIA and carbon nanotubes can be confirmed. Carbon nanotubes (4–5 wt%) will promote the conductivity of doped PANI from $1.4\text{--}1.9 \times 10^5\text{ ohm/m}^2$ to $8.0\text{--}10.0 \times 10^4\text{ ohm/m}^2$ of the PANI/CNT composite, while the more extent promotion happens to aniline/AIA copolymer from $2\text{--}8 \times 10^6\text{ ohm/m}^2$ to less than 10^4 ohm/m^2 . Moreover, TGA curves in Figure 5 indicate that carbon nanotubes show a slight improve in the thermal stability of the copolymer. The weight loss of the copolymer and its composite is three-stepped, the first and the third peak temperature are promoted by carbon nanotubes.

Conclusions

Polyaniline and aniline/AIA copolymer have been successfully synthesized via oxidation polymerization, as well as their composites containing carbon nanotubes. Spectrometric investigation confirms the doped structure of PANI and free charge carriers induced by carbon nanotubes. PANI/CNT composite exhibits both enhanced conductivity and thermal stability.

AIA can benefit the formation of a quinoid ring in the aniline polymerization and promote the conductivity of the copolymer. IR and Raman spectra reveal AIA/aniline

copolymers have both benzenoid and quinoid rings, as well as doped structures. Carbon nanotubes can promote the content of quinoid rings in the copolymer, and enhanced conductivity and thermal stability, simultaneously. It is also worth pointing out, copolymerization of AIA with aniline and the introduction of carbon nanotubes show a synergistic enhancement on conductivity.

Acknowledgements

This research was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Programs funded by the Ministry of Science and Technology of Korea. Xin Wang thanks the postdoctoral program of Chonbuk National University for a grant (2004).

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