

Conductive Plastics with Hybrid Materials

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Received 17 February 2009; accepted 9 April 2009

DOI 10.1002/app.30767

Published online 23 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Hybrid materials of conducting polyaniline (PANi) and multiwalled carbon nanotubes (CNTs) were synthesized using an in situ polymerization method. The resulting CNTs with a thin layer of PANi coating were further compounded with polypropylene to produce electrically conductive composite material. The PANi coating was found to enhance the CNT dispersion in PP. An amphiphilic component was also used as a surfactant to further enhance the dispersion. With these methods and materials, a conductivity of 26 S cm^{-1} was obtained. The conductivity of the hybrid material far exceeded that of the separately com-

pounded mixture and of that prepared of lower aspect ratio conductive materials: carbon nanofibers and carbon black. The level of conductivity qualifies the material for use in applications requiring electromagnetic interference shielding. By adjusting the PANi loading, the conductivity can be tuned down to obtain materials suitable for electrostatic discharge applications. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1494–1502, 2009

Key words: composites; conducting polymers; poly(propylene) (PP)

INTRODUCTION

Since the 1991 Nature article by Iijima,¹ the number of articles published on carbon nanotubes (CNTs) and CNT-related materials has exploded. CNTs still continue to be a target of intensive scientific interest, new applications and derivatives of the CNTs are sought after and put into commercial use. Conductivity-based applications of CNTs include flat-panel displays, scanning probe microscopes, lithium ion batteries, and sensing devices. A majority of applications and application prospects are based on the extraordinary mechanical and conductive properties of CNTs.^{2–4} The growing number of commercial applications have led to an increase of producers, produced amounts, and rapid price decline.

CNTs are attractive candidates for conductive plastic compounds. Their high conductivity, stability and high-aspect ratio among other desired properties are a good starting point to develop high-conductive plastic compounds. As an example for electromagnetic interference shielding, the material volume resistivity is typically $<1 \text{ } \Omega \text{ cm}$.⁵ CNTs can also be considered as fillers, but their unique structural, mechanical, electronic and thermal properties make them more than that. They are attractive building blocks for the development of novel polymer-nanocomposite materials with enhanced

conductivity.⁶ The potential use of this type of hybrid materials is not limited only to conductive plastic composites. PANi-CNT hybrids are potential materials also in fuel cells, batteries, biosensors, and printable electronics as well.

To be able to use CNTs as plastic additives to obtain conductivity and yet at the same time maintain the plasticity of the material, sufficiently small amounts of CNTs need to be used and these small amounts need to be well dispersed. The challenge associated with achieving good dispersion of nanotubes in polymeric matrices comes from the tendency of CNTs to agglomerate, that is, to form more or less spherical bundles and knots with dimensions from tens of nanometers up to hundreds of micrometers. With relatively large, spherical agglomerates, the percolation threshold for conductivity is 10-fold multiplied and the potential of the CNTs is thereby lost. To solve the problem, the agglomerates need to be separated into individual particles and preferably the self-affinity reduced. Also, the compatibility of the CNTs with the matrix needs to be improved in terms of surface polarity and intermolecular compatibility.⁷ Use of coatings and/or surfactants based on electrostatic interactions appear as best alternatives for good dispersion. Using this method, it is possible to avoid costly chemical covalent modifications of the CNTs.

On the other hand, the conducting polymers are interesting materials in composites by their economics, suitability for standard melt processing equipment, electrical and chemical stability and blendability with bulk polymers with moderate mechanical and other properties.⁸ The electrical conductivity of PANi is

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Contract grant sponsor: EC.

typically in the area of 10^{-5} to 10^{-9} S cm $^{-1}$ and a maximum reported value is 5 S cm $^{-1}$ which is one of the lowest among the common inherently conductive polymers.⁹ Because of the polymeric nature of PANi the percolation threshold when mixed in thermoplastic is adjustable, as opposed to when using ordinary fillers. CNTs functionalized with polymers have also been found to give better dispersion of CNTs in the polymer matrices of nanocomposites.^{10,11}

The plasticizing induced by the functionalized dopant is often not enough to reach homogenous dispersion in the matrix. This problem can be solved by using additional components to improve the compatibility of polyaniline with the matrix. One of the most efficient methods to improve compatibility of PANi with thermoplastics is the addition of compatibilizers, in particular, the ester derivatives of gallic acid. The intermolecular compatibility between the gallates and polyaniline units, and on the other hand, between gallates and polypropylene make these compounds excellent PANi solvents in the melt. Therefore, besides plasticizing the polyolefin matrix, they act as dispersants for PANi with many thermoplastics, particularly in the polyolefins. By selecting the type of the gallates properly, it is possible to surpass percolation threshold with as low-PANi concentration as 2–3%.^{12,13} Fryczkowski et al.¹⁴ showed that the conductivity of PP/PANi composites with lauryl gallate as the plasticizer depends on the gallate content.¹⁴

Extensive scientific interest has been focused on the combination of PANi and CNT. The common method to produce these composites is polymerization of PANi in the presence of CNTs. Conductivities higher than 15 S cm $^{-1}$ have been measured with 8% SWNT in PANi.⁸ These PANi/CNT composites have wide application potential for example in printable electronics. Less attention has been paid in applying these PANi/CNT materials to develop conductive thermoplastic composites with commodity matrices.

In this work, we successfully used PANi-coated MWCNTs and additionally amphiphilic surfactants for good dispersion and subsequently good conductivity. Our work also shows that the morphology, that is, the aspect ratio of CNTs plays a major role and is more suitable than that of the carbon black or carbon nanofibers (CNFs) for producing conducting hybrid materials.

EXPERIMENTAL

Materials

Multiwalled CNTs with purity >87% were purchased from NanoCyl SA, CNFs from Electrovac and carbon black "Printex XE2" (CB) from Degussa. Alkylphenol-

ethoxylate, 2-ethylhexanoic acid from BTC Specialty Chemical) was used as dispersing agent. In reactions phenol sulfonic acid (PSA, 65% water solution) from Synthetic Chemicals was used as counter ion in reaction, which was oxidized using ammonium persulfate (APS) from Degussa and aniline from Alcolac.

For compounding, Domolen 2600M (Domo Chemicals), a polypropylene with MFI 7.5 was used as a matrix material. The surfactant compounds were ethyl gallate, lauryl gallate, catechol, octadecyl gallate, and hexylresorcinol obtained from Sigma-Aldrich. Structures of these molecules are presented in Table I.

In situ synthesis

Aniline was polymerized using chemical polymerization in the presence of CNTs in a 1 L round flask equipped with a Teflon coated semi-circular adjustable speed mixer and ice bath. In the first processing step, 9 g of CNTs were dispersed to 200 g water containing 100 μ L of dispersing agent using stirring over night and subsequently ultrasonic for 20 min (mixture A). PSA-solution (8.63 g) was dissolved in water (400 g) and mixed for 30 min. Aniline (3 g) was added to the reaction mixture and mixed for 30 min. Then, the reaction mixture was cooled to 5°C, the mixture A was added and the mixing was continued for an additional hour. After this, 7.4 g of APS in 20 wt % water solution was added and the reaction was stirred for an additional 1 h in reaction temperature and at least 2 h in room temperature. The product was filtered with a Büchner-filter and Whatman GF-A glass fiber filter, washed and filtered three times with water. The product was dried in temperature below 40°C. The MWCNT-PANi product is marked as H1.

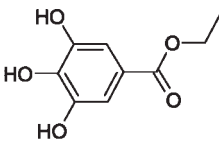
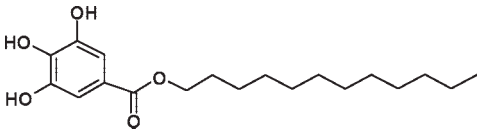
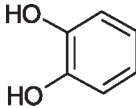
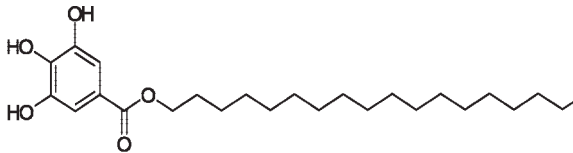
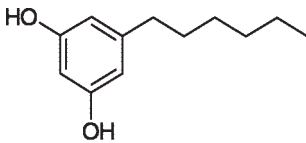
The coating of CNF and CB were performed similarly as the coating of MWCNT, resulting in hybrids H2 and H3, respectively.

Compounding experiments

Compounds were prepared according to the method described below of hybrid materials listed earlier.

A 6.00 g compound of electrically conductive PANi-nanoparticle-hybrid, selected substituted aromatic compound, and polypropylene was mixed in a miniature, co-rotating conical twin-screw extruder (Haake) at a temperature of 200°C for 1 min at a screw rotation speed of 100 rpm. The resulting compound was discharged in a miniature injection molding machine and further molded into rectangular samples with dimensions (mm) 1 mm \times 10 mm \times 60 mm at 220°C with a mold temperature of 40°C, injection pressure 350 bar (3 s), and post pressure of 160 bar (5 s).

TABLE I
Molecular Structure of Surfactants

Subst. aromatic compound	Formula
Ethyl gallate (EG)	
Lauryl gallate (LG)	
Catechol (CA)	
Octadecyl gallate (OG)	
Hexylresorsinol (HR)	

Characterization

Physical and chemical properties of the hybrid powders and the polypropylene blends were characterized, including SEM, FTIR, conductivity, and resistivity measurements.

SEM analysis

The morphology of pure dried hybrid powders and injection molded samples were studied by SEM. The sample surface was coated with gold to prevent the surface charging. Gold film thickness on sample surface is 50–70 nm. Analyses were made using JEOL JSM T100 with a voltage of 25 kV.

FTIR analysis

FTIR spectra of the hybrids and reference materials in powder form were recorded with a PerkinElmer FTIR Spectrum BX equipment with a wavelength from 400 to 4000 cm^{-1} using tablets prepared with KBr in a Specac tablet press.

Surface conductance

Surface conductance was calculated from the surface resistance of the dried hybrid powders, measured

from tablets with a diameter of 13 mm and thickness of 0.5–1 mm made with a Specac tablet press. Five tablets per sample were used for statistical reliability. Surface resistance measurements were done using a Finest 703 True RMS multimeter with pin-point measurement probes with a gap of 10 mm. Because of the dry and brittle composition of the material, it was not possible to prepare specimen for four-point measurement of conductivity. However, the method used here is indicative of the actual conductivity of these powders.

Volume conductivity

The electrical conductivity of the resulting injection molded samples was measured with a four-point probe method according to ISO 3915, adapted to suit the sample dimensions. Before measurement, the surface resistance was minimized by filing off the "skin" produced by the injection molding procedure and painting silver electrodes on the surface. Keithley multimeter was used for input voltage and current measurement, whereas Fluke 87 V was used to measure the voltage. The resistance is calculated from eq. (1).

$$R = U/I \quad (1)$$

TABLE II
The Conductivities of the Hybrids and the Carbon Starting Materials

Sample	Carbon starting material	Conductance (S)
H1	CNT	0.1
H2	CNF	0.2
H3	CB	0.2
PANi	–	0.001
MWCNT	CNT	0.2
CNF	CNF	0.2
CB	CB	0.1

The volume resistivity ρ was calculated using eq. (2)

$$\rho = RA/d \quad (2)$$

where A is the cross-section of the sample (1 mm \times 10 mm) and d is the distance of the voltage electrodes from each other (26 mm). The volume conductivity δ is the inverse of ρ .

RESULTS AND DISCUSSION

Conductance measurements and SEM studies of hybrid powder materials

The conductances of the black powder hybrids are shown in Table II. Black color in hybrid products is due to a specific color of CNTs and other carbon powders. The intensity of the black color overruns the specific green color, which PSA doped PANi has in conducting (emeraldine) form.

Despite the fact that the surface conductance of pure PANi-powder tablet surface was 0.001 S, the hybrid conductances were not on this low level, indicating that the hybrid conductance is mainly based on CNT conductance. This was probably due to the partial coating of the CNTs by PANi.

SEM images with enlargement of 15,000 of pure uncoated CNTs, CNFs and CB and respective hybrids with PANi are shown in Figure 1. In Figure 1(A), the difference between bundles of separate

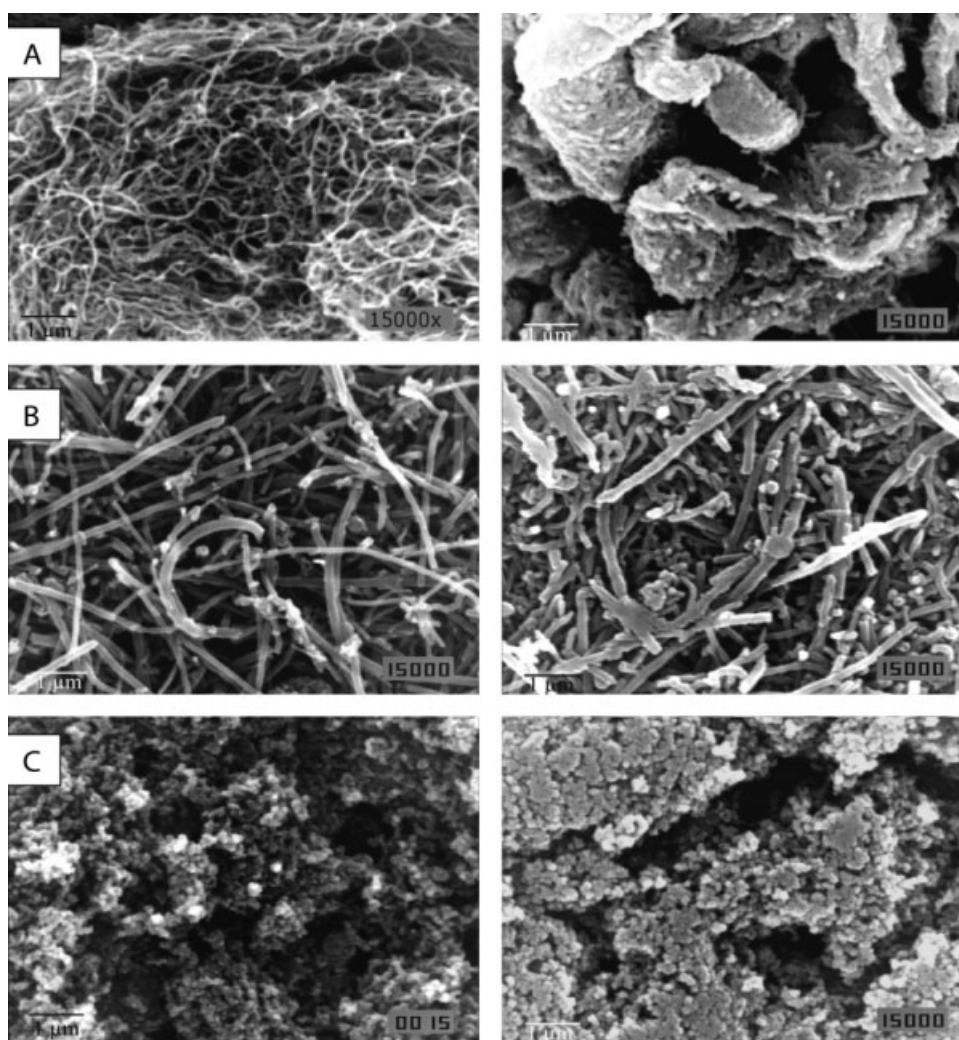


Figure 1 SEM-images with 15,000 enlargement of CNT starting material (A, left), H1 (A, right), CNF starting material (B, left), H2 (B, right), CB starting material (C, left), and H3 (C, right).

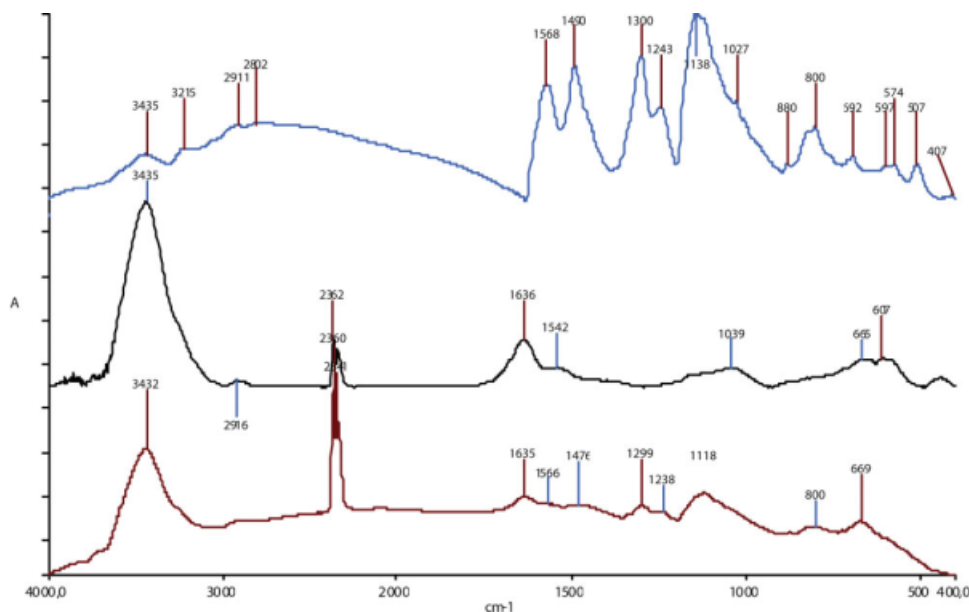


Figure 2 FTIR-spectra of **H1** (down), pure CNT (middle), and PANi-powder (top). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

uncoated CNTs (left) and PANi coated CNTs (right) can be seen. In Figure 1(A) (right) image of bundles of CNTs and some individual tubes covered with PANi in **H1** are seen. In Figure 1(B) (left) of pure CNFs appearance is more loose and stick-like than pure CNTs. In the image of the CNF-PANi hybrid material **H2** in Figure 1(B) (right), the PANi appears to be located around individual fibers. In Figure 1(C) of the CB (left) and **H3** (right), the lower aspect ratio in comparison with CNT and CNF is clearly visible. In Figure 1(C) (right) with **H3** even the PANi

coating is quite hard to be seen in surface of the spherical material. Still there are some areas where spherical particles seem to be partially sintered together, which indicates PANi in between particles.

FTIR spectroscopy for powders

FTIR-spectra of the carbon starting materials and the hybrids before compounding are presented in Figures 2 and 3. The peaks corresponding to polyaniline present in spectra of pure PANi and hybrid

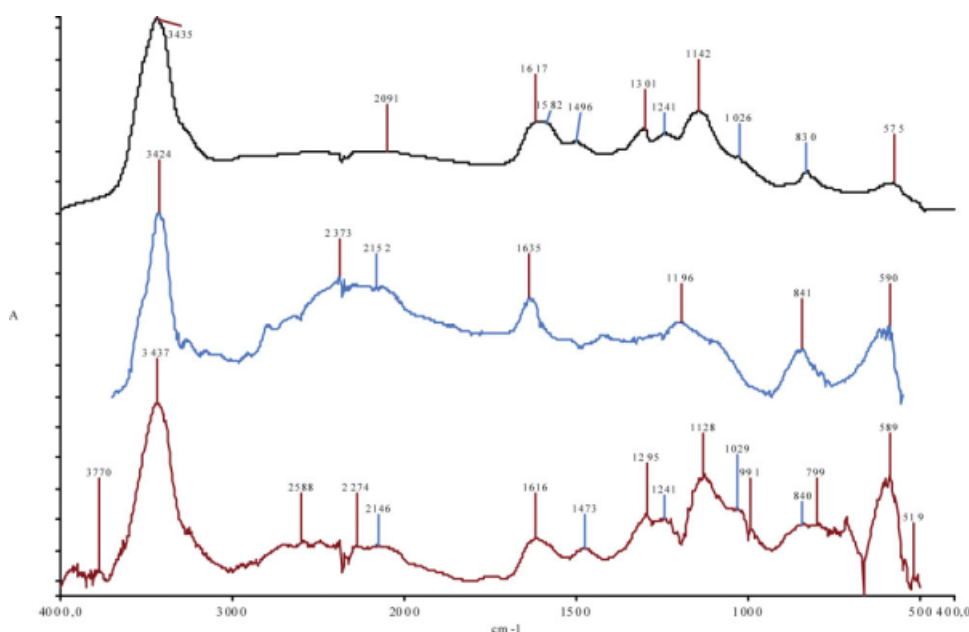


Figure 3 FTIR-spectra of **H3** (top), pure CNF (middle), and **H2** (down). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

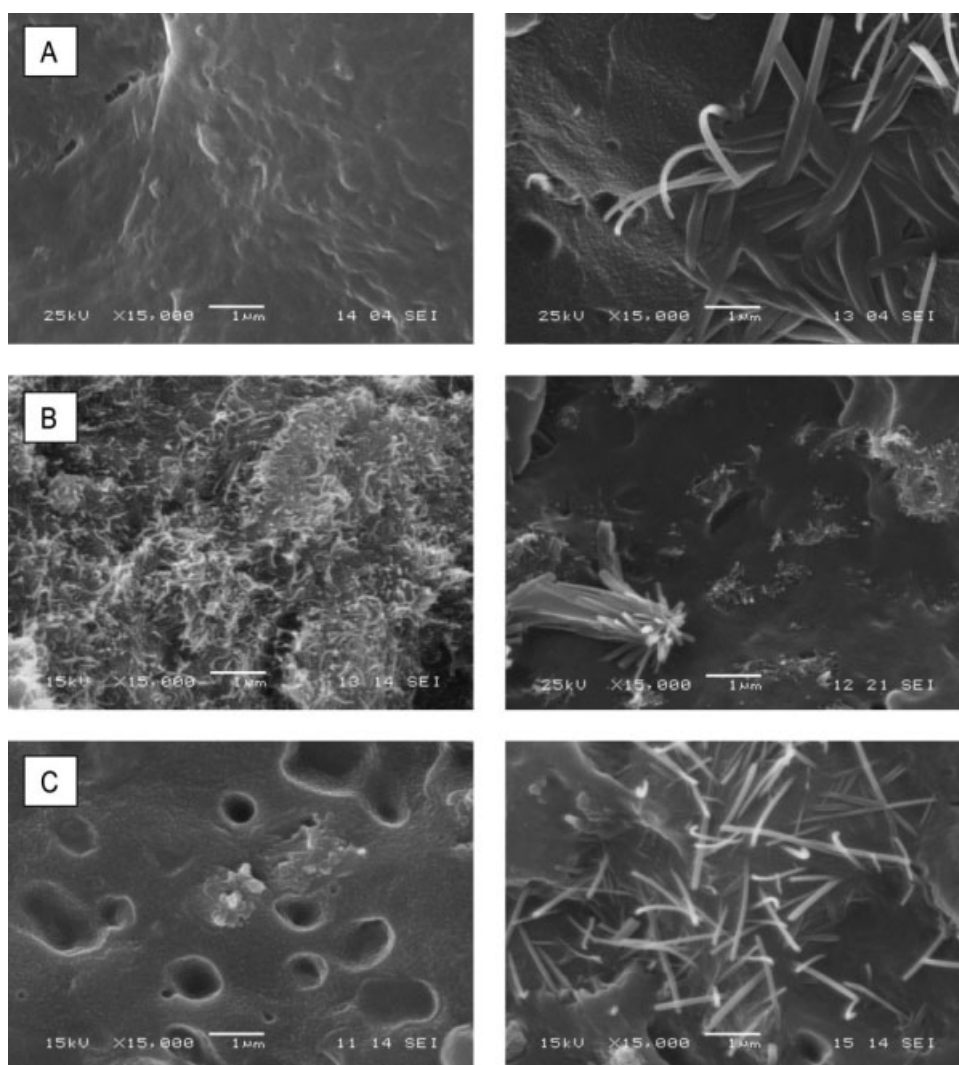


Figure 4 SEM-images with 15,000 enlargement of injection molded PP compounds. A (left) is neat PP, A (right) PP with 20% EG, B (left) PP with 10% CNT, B (right) PP with 10% CNT and 20% EG, C (left) PP with 10% PANI and C (right) PP with 10% PANI and 20% EG.

powders are benzene ring and quinone deformation peaks in about $1470\text{--}1490\text{ cm}^{-1}$ and about $1555\text{--}1590\text{ cm}^{-1}$. The peaks in the area $1295\text{--}1300\text{ cm}^{-1}$ and $1232\text{--}1235\text{ cm}^{-1}$ are assigned to C–N stretching linked to quinone and benzene ring secondary aromatic amine. In the region of $1010\text{--}1170\text{ cm}^{-1}$, characteristic of the aromatic C–H in-plane bending, peaks are also observed.

When comparing the spectra of pure PANi and CNTs (top and middle) to **H1** (down) in Figure 2 only peaks that are characteristic for CNT and PANi can be found. This indicates that no chemical bonding between PANi and CNT is formed and PANi is connected to the surface only with electrostatic interactions. Same phenomenon is seen also in Figure 3, when comparing the spectra of the components in the hybrids **H2** (down) and **H3** (top) to the CNF (middle) and PANi (Figure 2 top).

SEM studies of polypropylene compounds

The hybrid materials produced by in situ polymerization were compounded in polymeric matrices (PP) both with and without a surfactant and injection molded to test bars. To test the efficiency of the surface treatments, compounds containing also unmodified MWCNTs and PANi-powder with and without surfactant were produced. A SEM study was made for injection molded test bars in aim to study morphology and carbon material dispersion in compounds. Those SEM images are presented in Figures 4 and 5.

Figure 4(A) (right) shows a fibril-like structure. The phase separation is also observed with LG as dispersing agent in the promotion of the conductivity in LDPE by Yang et al. and in PP by Fryczkowski et al.^{13,14} Micrograph of composite with PP and CNT shows objects, which are probable CNT bundles

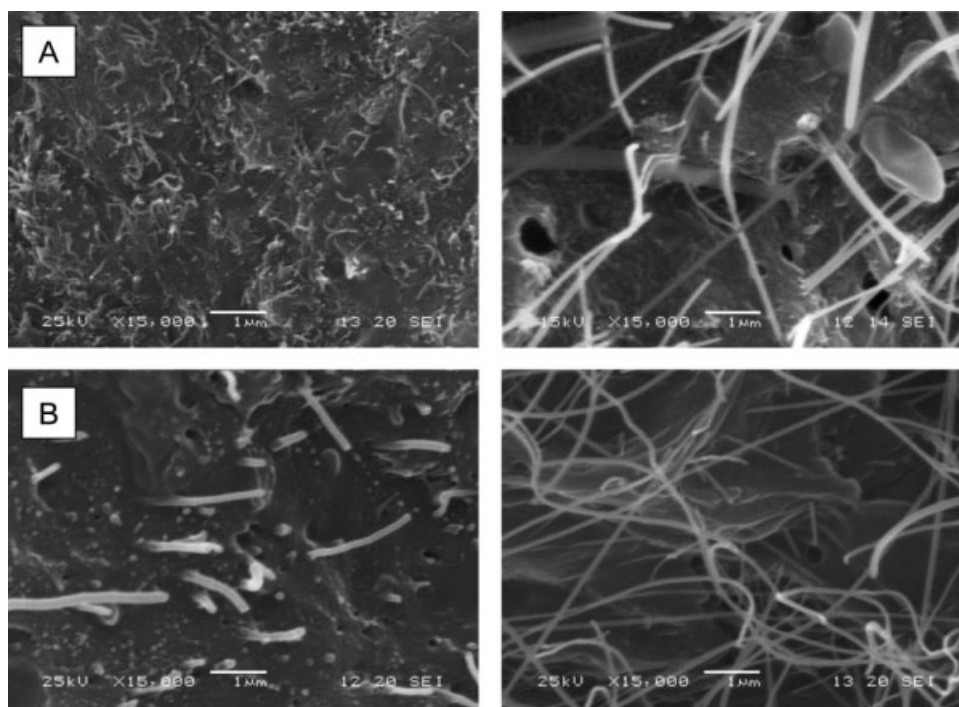


Figure 5 SEM-images with 15,000 enlargement of injection molded PP compounds with hybrid fillers. A (left) PP with 10% H1, A (right) PP with 10% H1 and 20% EG, B (left) PP with 10% H2 and B (left) PP with 10% H2 and 20% EG.

[Figure 4(B), left]. When ethyl gallate is added in PP-CNT-system, observable amount of CNT is lower and nanotubes are less homogenous distributed in this micrograph. The figure shows a separated EG phase.

The PP-PANI system, Figure 4(C) (left), there is observable small PANi particles, diameter $\sim 0.2\text{--}0.3\ \mu\text{m}$ forming agglomerates with a diameter $\sim 1\ \mu\text{m}$. The figure shows a number void like objects, which may originate from PANi agglomerates. If this assumption is valid, the distribution of PANi agglomerates is quite homogenous. When ethyl gallate is added in composites, the morphology passes a transformation, Figure 4(C) (right). The structure is dominated by EG fibrils.

Figure 5 presents micrographs of PP composites with hybrid fillers consisting long aspect ration carbon particles. The composite with PANi-CNT-hybrid (H1), Figure 5(A) (left), shows quite homogenous distributed hybrid particles on surface, although there are regions with low amount of hybrid filler. When ethyl gallate is added in system, fibrils are observable. The figure includes some flake like objects, which can be EG crystals. When conductive hybrid includes CNFs (H2), Figure 5(B) (left), these hybrid fiber are well observable. Adding ethyl gallate in the system, the results are a structure where fiber-like objects dominates the picture.

The viscosity of low-molecular weight gallate molecules is essentially lower compared with the melt viscosity of PP. Observed fibril like objects may be

explained by shear deformation of gallate phase during molding. Furthermore, differences between these fibril objects are observable in samples with different compositions and gallate as well as hybrid contents. Addition of hybrids in the system changes the viscosity of the gallate phase, partly due to the molecular recognition between these components. These factors affect the shape and size of the gallate fibrils on the fractured surfaces. However, these micrographs do not allow the analyses of the gallate phase morphology in details and to get statistically reliable results. The details of the changes in the phase morphology and the subsequent effect on the gallate fibrils are a topic which will be discussed in detail in a further publication.

Conductivity of polypropylene compounds

The electrical conductivities of compounded and injection molded samples are shown in Table III.

In our experiment, the CNT compound with 10% loading in PP without dispersing additive has no conductive characteristic. When the compound includes 10 wt % LG, the conductivity increased up to value of $8 \times 10^{-2}\ \text{S cm}^{-1}$.

Compounds with PP and 10% loading of pure PSA-doped PANi-powder and mixture of the PANi-powder with CNT gave only very low-conductive values. EG addition increased the conductivity only one decade to $1 \times 10^{-8}\ \text{S cm}^{-1}$.

TABLE III
Compounds Prepared of CNT, H1, H2, and H3 Hybrids and PANi

Compound	Conductive material	Subst. aromatic compound	Subst. aromatic compound (%)	PP (%)	Conductive material/PP (%)	Volume conductivity (S cm ⁻¹)
1	CNT	–	–	90	11.1	10 ⁻¹⁰
2	CNT	EG	10	80	12.5	8.0 × 10 ⁻²
3	CNT	EG	20	70	14.3	2.6 × 10 ⁻³
4	H1	–	–	90	11.1	10 ⁻¹²
5	H1	EG	10	80	12.5	10 ⁻¹¹
6	H1	EG	20	70	14.3	26
7	H1	EG	30	60	16.7	15
8	H1	LG	10	80	12.5	2.6 × 10 ⁻²
9	H1	LG	20	70	14.3	1 × 10 ⁻¹
10	H1	LG	30	60	16.7	3.7 × 10 ⁻²
11	H1	OG	20	70	14.3	1.7 × 10 ⁻¹
12	H1	CA	20	70	14.3	1.5 × 10 ⁻⁴
13	H1	HR	20	70	14.3	2.2 × 10 ⁻³
14	H2	EG	20	70	14.3	10 ⁻¹¹
15	H3	EG	20	70	14.3	10 ⁻¹¹
16	PANi	–	–	90	11.1	10 ⁻⁹
17	PANi	EG	20	70	14.3	10 ⁻⁸
18	CNT and PANi	–	–	90	11.1	10 ⁻⁹
19	CNT and PANi	EG	20	70	14.3	10 ⁻⁸

The loading of conductive materials in all samples were 10 wt %.

The conductivity of **H1** hybrid with 10 wt % loading without dispersing agent did not show conductive characteristic. The polyaniline itself is not capable to create substantial dispersive conditions in this system. The addition of 10 wt % of EG has no essential effect on the measured conductivity. The increase of the EG content above this level has a crucial effect. The conductivity with 20 and 30 wt % EG reached conductivities of 26 and 15 S cm⁻¹, respectively. When the EG was replaced by LG with a longer alkyl chain, the effect was similar to that observed in the case of increasing the EG weight content above 10 wt %. The amount of 10 wt % of LG was sufficient to result in dramatic improvement in conductivity. However, the measured conductivities with 20 and 30 wt % gallate loading were one or two decades weaker than in the case of EG. Results of Fryczkowski et al.¹⁴ gives maximum conductivity for PANI-PP compound as a function of LG loading with 10% loading. The OG with an even longer alkyl tail, showed by 20 wt % loading a similar effect on conductivity that was measured in the case of other gallates.

The two other molecules used, CA and HR, both have similar functional groups to the gallates (Table I). The use of these molecules at 20 wt % loadings increased the conductivity. However, the measured conductivities were at least two or three decades lower than those with gallate surfactants.

To test the effect of starting material carbon quality, that is, the aspect ratio on the conductivity properties, hybrids with CNF and CB were produced with 20 wt % EG. Contrary to compounds of **H1**

with the same EG content, material with good conductivity was not obtained. The differences in particle aspect ratio of CNT, CNF, and CB appear to have effect on the blended end-product conductivity. The presence of PANi connected to carbon material has also an effect on the end-product conductivity by enhancing the miscibility of the carbon material and creating conductive bridges between carbon particles. However, PANi-particles mixed as powder form with CNT do not have the similar effect.

Several substituted aromatic surfactants with varying alkyl chain tails were tested with the **H1**. The results show that a long alkyl chain tail in the surfactant is not a prerequisite, but beneficial in attempt to achieve good conductivity levels in polypropylene matrix. As previously shown, the amphiphilic molecules, such as gallates, can act as surfactants, dispersing the PANi into the polyolefin.¹¹ When using fibrous particles with extremely high-aspect ratio and resulting high-length-volume ratio such as the CNTs, the same mechanism of dispersion applies and a very good mixture with conductive pathways is created. Despite their relative weakness, the hydrogen bonding and electrostatic interactions between both the surfactant hydroxyl groups with PANi and the surfactant alkyl tail with the polyolefins are sufficient to result in effective dispersion. This is due to the high amount of these interactions per coated PANi chain and the low volume of the underlying CNTs.

The surfactants with hydroxylic substituents in the 1 and 2-positions (gallates and catechol) were favored over the surfactants with these substituents

in the 1,3-positions (resorcinol). This can be explained by the ability of the 1,2-substituted surfactants to function as double hydrogen bond donors to one acceptor in the conducting PANi-polymer chain, whereas the compounds with hydroxyl groups in 1,3-positions can only donate hydrogen bonding from one donor hydroxyl group per PANi polymer acceptor group (Table I).

CONCLUSIONS

Coating CNTs with PANi by in situ polymerization is a suitable method for preparation of high-conductive hybrid materials for dispersion of the nanotubes inside polymeric matrixes, such as polypropylene. In the synthesized hybrids, the carbon conductivity dominates; measured conductivities were essentially higher than those observed in pure emeraldine PANi. The aspect ratio and diameter of the coated conductive particles apparently plays a critical role in determining the final conductivity of the compound with the matrix polymer. With relatively low-aspect ratio and thick diameter materials—for example carbon black (CNFs)—the dispersive coating is not sufficient to result into a highly conductive network. The use of pure PANI or PANi-coated substrates with lower aspect ratio, for example, carbon black or CNFs, did not yield similar conductivity levels as CNT hybrids when blended with PP.

The PANi coating provides a template for the molecular recognition that disperses the PANi-coated CNTs in the polyolefin matrix in the presence of gallates: the hydroxylic functionalities of the gallates tie the CNTs to the nonpolar matrix by the alkyl tail chain.

Even better dispersion and subsequent conductivity was obtained using substituted aromatic surfactants in the compounding. Highest conductivities

were measured by composites with ethyl gallate as dispersing additive. SEM micrographs showed differences in morphology of samples. Thus, the used methods do not allow make detailed conclusions about effects of observed morphology on measured conductivity. A complementary work is needed to create this overview.

This work has been carried out in European IP project Poly-Cond (IP 515835-2). The financial support is gratefully acknowledged.

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