

Photoluminescent Carbon Nanocapsule/Polycyanate Composites with Hydrogen Bond Interactions

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ABSTRACT: Dispersion of carbon nanocapsules (CNC) in a liquid aromatic dicyanate, 4,4'-ethylenediphenyldicyanate (LECy), and in the polycyanate (PCn) resin, derived from the subsequent cure of LECy, was attempted in this study. CNC was primarily oxidized to introduce carboxylic acid groups to yield carboxylated CNC (CNC-COOHs), which can then be dispersed in the monomeric LECy through hydrogen bond (H-bond) interactions between —COOHs in CNC-COOHs and cyanate (—O—C≡N) groups in LECy. Upon heating, the constituent LECy proceeds to polycyclotrimerization to generate a PCn resin, with *s*-triazine rings as the crosslinking points. Here, the inherent *s*-triazine rings serve as H-bond sites to —COOHs in CNC-COOHs and effectively promote the homogeneity in the resulting CNC-COOHs/PCn composites; further, the H-bond interactions were confirmed by infrared spectroscopy. The CNC-COOHs clusters in the liquid LECy were characterized using light scattering, to reveal a wide-range of size

distribution with a mean diameter of 278 ± 25 nm. Transmission electron microscopy (TEM) was further applied to show the well dispersion of CNC-COOHs clusters in the PCn matrix phase of the resulting composite. The absorption and emission spectra of the resulting CNC-COOHs/PCn blend were also determined to show their characteristic properties of the photoluminescence (PL) of CNC-COOHs and PCn components. The emission spectrum of the resulting CNC-COOHs/PCn blend was bathochromically shifted compared with the pure PCn. This energy-transfer process is due to π - π electron overlapping of aromatic ring between the PCn matrix and the CNC-COOHs, resulting in the extended conjugated lengths. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3784–3788, 2006

Key words: curing of polymers; fluorescence; carbon nanocapsules; nanocomposite

INTRODUCTION

Carbon materials, such as fullerene (C₆₀, C₇₀, and higher analogs), carbon nanotubes (CNTs), and carbon nanocapsules (CNC), have been widely applied in various applications, including gas separation, water purification, catalyst support, electrodes for electrochemical devices, optical emitting devices, and also used to improve electrical conductivity and electrostatic charging behavior.^{1–4} To extend the potential applications of carbon materials, composites combining both carbon materials and polymers were prepared to acquire the potential merits, such as high aspect ratio, high mechanical strength, thermal stability, and conductivity.^{5–6} Polymeric composites, incorporating fullerenes or CNTs, had been extensively evaluated;^{7–9} however, CNC-related composites still lacks. CNC can be considered materials with proper-

ties in-between fullerene and CNTs; therefore, development of CNC/polymer composites is worthwhile from either academic or practical considerations. To make a carbon material/polymer composite, two main problems need to be overcome: (i) uniform dispersion of carbon materials in the polymer matrix without aggregation, and (ii) enhanced interface adhesions between carbon materials and polymers. Strategies, e.g., chemical modification by introducing functional groups (—Br, —COOH, —CH₃ etc.), used in the CNTs systems may well be applied to solve the aggregation problems in CNCs,¹⁰ since CNTs materials are difficult to be dispersed in considering their large contact surface areas. Previously, Chen et al. successfully introduced carboxylic acid (—COOH) groups into shortened single-walled nanotubes (SWNTs) by oxidizing with strong acids. This oxidized SWNTs can be further treated with thionyl chloride and octadecylamine, to generate materials soluble in common organic solvents.¹¹ Wong et al. demonstrated that oxidation of CNTs by acid pairs (H₂SO₄/HNO₃) can introduce carboxyl acid groups on the surface of CNTs.¹² Polycyclotrimerization of aromatic

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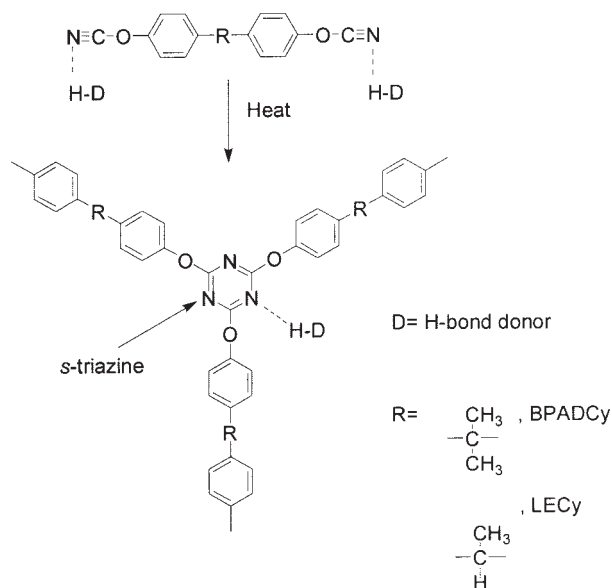


Figure 1 Polycyclotrimerization of the aromatic dicyanates and the potential H-bond sites in the starting dicyanates and in the derived PCn.

dicyanates (Fig. 1) is unique in considering that this reaction brings three cyanate groups to form a *s*-triazine ring as the crosslinking point in the resulting polycyanates (PCn) network.¹³ The PCn resins have high thermal stability, low dielectric constant, good mechanical properties, etc. Previous study^{14,15} suggests that both the cyanate ($-\text{O}-\text{C}\equiv\text{N}$) groups in the starting monomer and the oxygen and nitrogen atoms around the *s*-triazine ring in the cured PCn resins are the hydrogen bond (H-bond) acceptors (cf. Fig. 1). It is to say, dicyanate monomers and the cured PCn can be used to homogeneously disperse materials having H-bond donating groups, which includes CNC with H-bond donating group, e.g., carboxylic acid.

In this study, CNC was first oxidized under acidic conditions to generate carboxylic acid-functionalized CNC (CNC-COOHs). CNC-COOHs were then dispersed by a liquid aromatic dicyanate, (4,4'-ethylenediphenyldicyanate (LECy), cf. Fig. 1), and the whole mixture was cured by heating, to generate CNC-COOHs/PCn composites. Here, liquid LECy monomer can be directly used as dispersion agent for CNC-COOHs, and in addition, PCn resin derived from LECy is PL material, just as the same for the resin derived from the bisphenol A dicyanate (cf. Fig. 1) counterpart reported previously.^{16,17} Therefore, the light emitting properties of the CNC-COOHs/PCn blend are described as well. The CNC-COOHs were dispersed in PCn matrix with inherent H-bond; further, the resulting CNC-COOHs/PCn blend was characterized by absorption and PL spectra, in an effort to recognize the photophysical properties.

EXPERIMENTAL

Materials

CNC was supplied by Industrial Technology Research Institute of Taiwan. LECy with purity greater than 99% was obtained from the LONZA Group Corp. Nitric acid, sulfuric acid, and potassium hydroxide were purchased from Aldrich Chemical Co. and were used without further purification. Tetrahydrofuran (THF) and toluene were vacuum distilled, after dehydration by sodium. Ethylene chloride was distilled from calcium hydride (CaH_2).

Instrumentations

A Biorad FTS-155 Fourier-transform infrared spectrometer was used to measure infrared spectra in the optical ranges of $4000\text{--}400\text{ cm}^{-1}$. Wide-angle X-ray diffraction (WAXD) was performed with a Siemens Diffractometer D5000 Model, with Ni-filtered $\text{K}\alpha$ radiation. A Philips CM-200 TWIN and Jeol TEM-3010 TEM were employed, to examine the interfaces between the second phase and matrix. Specimens were embedded in a cured epoxy resin, and sectioned to 50 nm thick by ultra-microtome (model: Reichert Ultracut E). UV-vis spectra were obtained from a Hitachi U-3501 spectroscopy. Emission spectra were obtained from a Lab Guide Fluorescence spectrophotometer.

Chemical reactions

Carboxylation of CNC and its further titration to determine the carboxylation numbers were performed, according to the literature procedures,^{11,12} and were described as follows:

Carboxylation of CNC and its titration

CNC (100 mg) was added to a 100 mL mixture of sulfuric acid/nitric acid (3/2 v/v). The solution was sonicated in a heating bath, at 65°C for 2 h. The resulting mixture was diluted with distilled water (500 mL) before further consecutive washing, with large amounts of distilled water, to the extent that no residual acid was detected. The resulting carboxylated product (CNC-COOHs) was carefully collected by centrifugation and dried before titration, to determine its carboxylation number. Ethanol (50 mL) was added to CNC-COOHs, and the resulting mixtures were bath-sonicated at 25°C for 1 h. A solution of 0.01N KOH (50 mL) was dropped in before sonication, for another 7 h. The resulting dispersion was titrated with 0.01N HCl solutions, to determine the amounts of the unreacted NaOH in the solution. Titration results are summarized in Table I.

TABLE I
Titration Results of the Carboxylated CNC^a

KOH added to CNC-COOH dispersion (mol)	HCl used for the titration of mixture (mol)	COOH concentration in the CNC (mol COOH/g CNC)
5×10^{-4}	3.2×10^{-4}	0.18×10^{-2}
5×10^{-4}	3.1×10^{-4}	0.19×10^{-2}

^a Sample weight of carboxylated CNC is 20 mg for titration.

Dispersion of CNC-COOH and LECy and its further curing

Calculated amounts of CNC-COOHs were dispersed in the liquid LECy monomer, through the use of sonication for 2 h at 25°C. CNC-COOHs/LECy mixtures of different compositions were then deposited on an aluminum disc, and heated at 250°C for 90 min under nitrogen. With this manner, cured CNC-COOHs/PCn composites, with weight ratios ranging from 1:0.001 to 1:0.016, were prepared, and their compositions were illustrated in Table II.

RESULTS AND DISCUSSION

The CNC-COOHs were precipitated upon addition of methanol to the acidic media, and were then centrifuged, collected, and sonicated in different media. As shown in Figure 2, the CNC-COOHs cannot be dispersed in dichloromethane, even with the help of sonication. On the contrary, CNC-COOHs can be dispersed well in THF, but agglomeration occurred after standing still for sometimes. To the best, homogeneous dispersion of CNC-COOHs in the viscous LECy liquid still remained, even after 24-h standing. The pristine CNC is totally unable to be dispersed in any of the aforementioned media; therefore, the enhanced dispersion of CNC-COOHs in LECy is supposed to be due to the H-bond interactions between $-\text{O}-\text{C}\equiv\text{N}$ in LECy and $-\text{COOH}$ in CNC-COOHs. Furthermore, the viscous LECy liquid may prevent the dispersive CNC-COOHs particles from agglomeration after standing still for 24 h. CNC-COOHs/LECy mixtures of different compositions were then deposited on an aluminum disc and heated at 250°C for 90 min (cyanate conversion > 90% as determined from differen-

TABLE II
Compositions of Different CNC-COOHs/PCn

PCn/CNC-COOHs (wt %)	$-\text{OCN}/-\text{COOH}$ (mol %)
1/0.1	1/0.12
1/0.4	1/0.53
1/0.8	1/1.05
1/1.6	1/2.12

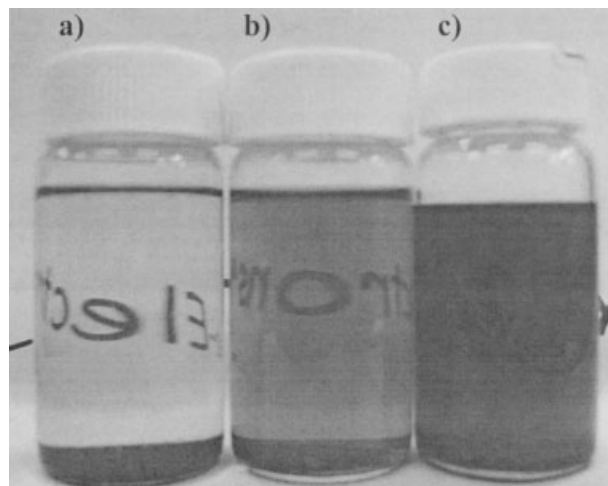


Figure 2 Dispersion of CNC-COOHs (0.02 wt %) in (a) dichloromethane, (b) THF, and (c) LECy after 24-h standing.

tial scanning calorimetry), under nitrogen atmosphere. The resulting CNC-COOHs/PCn composites were subjected to FT-IR investigation, as revealed in Figure 3. Pure CNC-COOHs showed the characteristic bands due to hydroxyl group (3400 cm^{-1}), and the carbonyl groups of the carboxylic acids in the monomeric (1712 cm^{-1}) and in the associated dimeric (1650 cm^{-1}) forms.^{18,19} An extra carbonyl stretching at 1750 cm^{-1} emerged and gained its intensity (relative to the $-\text{CH}$ and $-\text{CH}_3$ stretching in the ranges of $2850\text{--}3000 \text{ cm}^{-1}$) with increasing CNC-COOHs content in the composites [indicated by arrows in Figs. 3(b)–3(e)]. Previously, carboxylic acid H-bonded to pyridine ring shows its $-\text{C}=\text{O}$ stretching at 1750 cm^{-1} ;^{20,21} there-

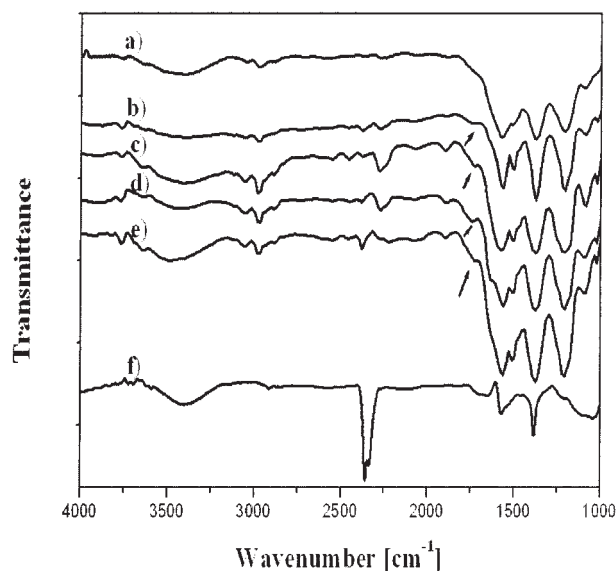


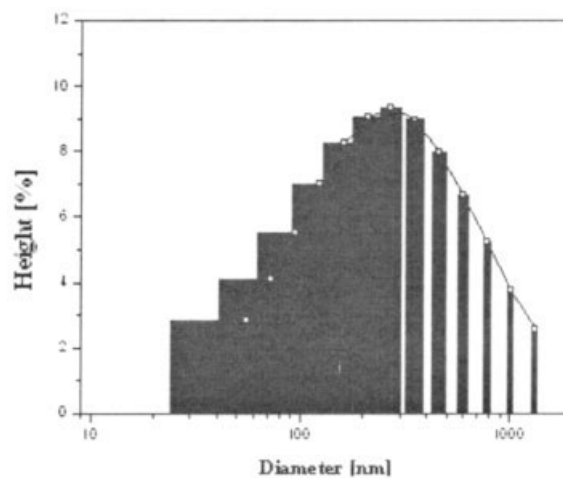
Figure 3 Infrared spectra of (a) the cured LECy and CNC-COOHs/PCn composites, with CNC-COOHs wt % of (b) 0.1, (c) 0.4, (d) 0.8, (e) 1.6, and (f) 100 (pure CNC-COOHs).

fore, this 1750 cm^{-1} band in the composites is due to the carboxylic acids H-bonded to the *s*-triazine rings in PCn. Our previous study,¹⁵ on the cured PCn and poly[(ethylacrylate)-*co*-(acrylic acid)] blends, also confirms the existence of the —C=O stretching of the carboxylic acid bonded to *s*-triazine ring, which is located around 1730 cm^{-1} . These strong H-bond interactions would promote the mutual miscibility between CNC-COOHs and PCn resin.

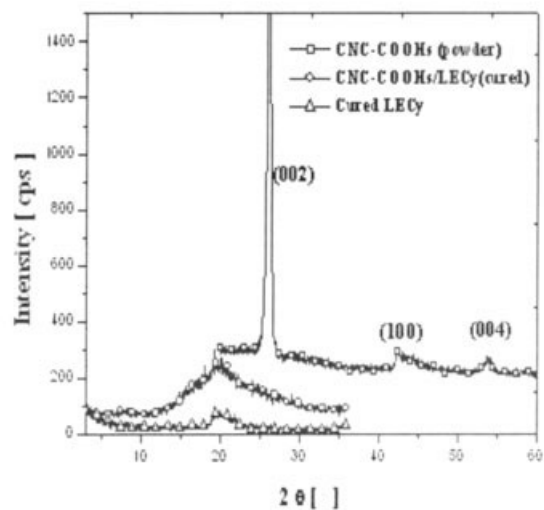
The cluster of the CNC-COOHs (0.02 wt %) in LECy was further characterized using light-scattering method [Fig. 4(a)]. The result showed a wide range of cluster size distribution, and a mean diameter of $278 \pm 25\text{ nm}$ was evaluated. The oxidized CNC-COOHs in this study carries only tiny amounts of —COOH moieties (9.5×10^{-3} mol of —COOH per gram of CNC-COOHs), and hence the H-bond interactions between the —COOH groups and the polar LECy are thereby limited. Further increase of the —COOH groups by prolonged oxidation of CNCs may be used to enhance the dispersion of the CNC-COOHs in LECy.

The CNC-COOHs, cured LECy, and CNC-COOHs/PCn (0.02 wt %) composite were characterized by WAXD in Figure 4(b). CNC-COOHs showed a diffraction pattern resembling the unoxidized CNCs, with the reported, (100) and (004), and the well-graphitized (002) diffractions.^{22,23} The cured PCn resin showed a broad diffraction peak around $2\theta = 20^\circ$, reflecting its amorphous nature. With the inclusion of small amounts of CNC-COOHs, the CNC-COOHs/PCn composite presents a diffraction pattern basically attributed to the PCn matrix. The absence of the CNC-COOHs diffraction in the composite may well be attributed to its dilute concentration in PCn matrix. The image of CNC-COOHs/PCn (0.02 wt %) from TEM was shown in Figure 4(c) and exhibited the presence of aggregated clusters of different sizes. Separate TEM micrograms showed that pristine CNC and the oxidized CNC-COOHs resembles each other in shape, which are virtually elongated ellipsoids, with the longest diameter ranging from 30 to 50 nm. Judging from the cluster sizes, as shown in Figure 4(c), we may suggest that the CNC-COOHs clusters of aggregation numbers ranging from two to six actually exist in the PCn matrix.

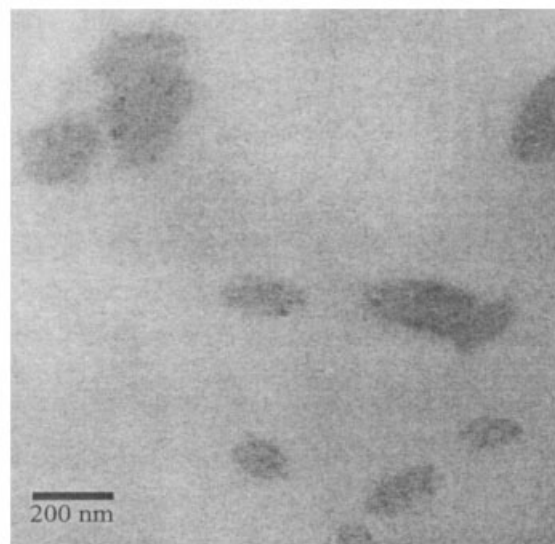
The absorption and emission spectra of the cured CNC-COOHs/PCn products, along with the pure CNC-COOHs and PCn components, are shown in Figure 5. The absorption result from CNC shows a main absorption centered at 300 nm. On the other hand,



(a)



(b)



(c)

Figure 4 (a) Particle-size distribution from the light scattering of CNC-COOHs (0.02 wt %) in LECy, (b) WAXD diffraction patterns of pure CNC-COOHs (\square), CNC-COOHs/PCn (\diamond), and the pure cured LECy (\triangle). (c) TEM image of CNC-COOHs (0.02 wt %) in PCn matrix.

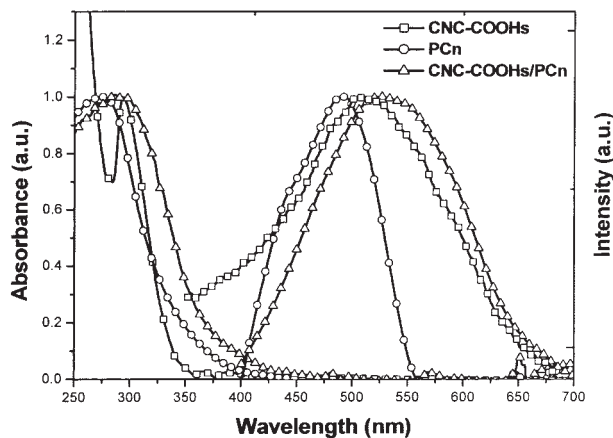


Figure 5 Absorption and PL spectra of the CNC-COOHs in THF solution, PCn film, and CNC-COOHs/PCn film state. PL was obtained as excitation at 300 nm.

LECy-derived PCn exhibits a broad absorption pattern, extending from 200 to 350 nm, just as the same with reported pattern.¹⁶ However, the absorption edge of the cured CNC-COOHs/PCn blend was broad compared with the pure CNC-COOHs and PCn, because of the π - π stacking of the aromatic ring between the CNC-COOHs and PCn. The strong emission was observed upon exciting the diluted pure CNC-COOHs in the THF solution at 300 nm, and the maximum emission was observed at 500 nm. When the cured CNC-COOHs/PCn blend was excited at 300 nm, it showed an emission spectrum in wide ranges of 400–700 nm, which was bathochromically shifted compared with the pure CNC-COOHs and PCn. This is due to the π - π electron overlapping between the aromatic ring of PCn and the CNC-COOHs, causing an increase in the π -conjugation lengths.²⁴

In conclusion, CNC can be successfully oxidized to obtain CNC-COOHs, which can be further dispersed by the reactive LECy monomer. The homogeneous CNC-COOHs/LECy mixtures were then cured to prepare CNC-COOHs/PCn composites. The inherent H-bond interactions between the carboxylic acid in CNC-COOHs and the *s*-triazine ring in PCn enhance the mutual miscibility between the two components. Light-scattering study revealed an average diameter of 278 ± 25 nm for the nanoparticle clusters inside the

composite, which suggests an average aggregation number of 2–6, which can also be evaluated from the corresponding TEM image. Finally, the resulting CNC-COOHs/PCn composites are actually PL materials because of the PCn matrix. Further exploration of the PL behavior is still undergoing in our laboratory.

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