ORIGINAL PAPER

# Morphological, electrical, thermal and mechanical properties of phthalocyanine/multi-wall carbon nanotubes nanocomposites prepared by masterbatch dilution

**Zicheng Wang · Xulin Yang · Junji Wei · Mingzhen Xu · Lifen Tong · Rui Zhao · Xiaobo Liu**

**Abstract** Multi-wall carbon nanotubes reinforced thermo-set phthalocyanine (Pc/CNTs) nanocomposites were successfully prepared through melt-mixing and masterbatch dilution and investigated for their morphologies and physical properties. Pc/CNTs nanocomposites were prepared by the more optimized masterbatch method. The feasibility of using Pc/CNTs nanocomposites was investigated by evaluating their electrical, dielectric, mechanical, morphological and thermal properties as a function of CNT loading. Consequently, the dramatic electrical and dielectric transition happened when CNT content was about 1 wt%. For the 1 wt% CNTs-filled Pc nanocomposites, a 51.4 % increase in flexural strength was obtained and flexural modulus was also improved from 3851.7 MPa to 3973.3 MPa. All Pc/CNTs nanocomposites showed high thermal and thermo-oxidative stabilities up to 535 °C. Pc/CNTs nanocomposites with multifunctional properties can find uses under some critical circumstances with requirements of high strength and temperature.

**Keywords** High performance polymers · Dielectric properties · Thermal stability · Carbon nanotubes · Masterbatch · Mechanical properties

Z. Wang · X. Yang · J. Wei · M. Xu · L. Tong · R. Zhao · X. Liu (✉)
Research Branch of Functional Materials, Institute of Microelectronic & Solid State Electronic, High-Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China,
Chengdu 610054, People's Republic of China
e-mail: liuxb@uestc.edu.cn

## Introduction

Phthalocyanine (Pc) polymers are a unique class of high temperature thermoset materials, which display good mechanical properties, superior flame and abrasion resistances, outstanding hydrolytic and oxidative stabilities, high char yield and chemical inertness, excellent thermal and thermo-oxidative stabilities [1–8]. Pc monomers can be easily melted and readily processed into shaped forms in the presence of curing additive to get high temperature Pc polymers [8]. Thus they are good polymer matrices which can be used to prepare advanced composites. Such composites have been showing a variety of potential uses for adhesive [1], electronic [2–4], and structural applications [5–7].

Carbon nanotubes (CNTs), due to their high strength (100 times stronger than steel) and modulus (about 1 TPa), high thermal conductivity (about twice as high as diamond), excellent electrical conductivity (1000 times higher than copper), and thermal stability (2800 °C in vacuum) [9–13], have been considered as one of the most promising fillers for preparing polymer nanocomposites with multifunctional properties. However, large-scale use of CNTs is hindered due to their poor dispersion states in matrices because of Van Der Walls and $\pi$–$\pi$ interactions [14, 15]. One of challenges in the preparation of CNTs-based nanocomposites lies in CNTs' uniform dispersion. At present, two different approaches are usually used to achieve good dispersion of CNTs: chemical methods and physical methods. Chemical methods, on the one hand, use surfactants [16] or functionalization [17] to change CNT surface energy, reduce the tendency to agglomerate in the matrices and thus lead to large improvements in the physical properties of the resultant nanocomposites. On the other hand, defects are preferentially observed at the open ends of CNTs in these methods [18]. However, physical dispersion methods such as

sonication, ball milling, grinding and high speed shearing, can maintain CNTs' nature merits and possess the potential large-scale industrial production. Among them, melt-mixing is most economically and environmentally viable since it does not require solvents, but low shear force can not provide suitable dispersion of CNTs [19, 20]. To achieve the target of uniform dispersion, secondary blend was used to enable uniform dispersion of CNT bundles in the polymer matrix through masterbatch dilution [21, 22]. During the first blend of masterbatch, high shear force can provide suitable CNT dispersion because CNT disentanglement is facilitated. More importantly, first blend of masterbatch can promote the compatibility between CNTs and polymer matrices. Thus, masterbatch technique is a simple and effective method to incorporate CNTs into polymer hosts.

To expand various advantages and applications of Pc and CNT materials, in the current work, CNTs were firstly coated by Pc monomer 4,4'-bis(3,4-dicyanophenoxy) biphenyl (BPH) to prepare BPH-treated CNTs: BPH/CNTs masterbatch. Then, the effect of blend method melt-mixing and masterbatch on the properties of Pc/CNTs nanocomposites were investigated. Consequently, Pc/CNTs nanocomposites prepared by masterbatch did show better CNT dispersion states and physical properties. Finally, the effect of CNT loading on the electrical, dielectric, mechanical, thermal properties of Pc/CNTs nanocomposites were investigated and discussed.

## Experimental

### Materials

Multi-walled carbon nanotubes (CNTs) (diameter: 10–30 nm, length: 3–10 μm, purity: >95 %), synthesized via chemical vapor deposition, was supplied by Chengdu Organic Chemicals CO. LTD. Chinese Academy of Science. Phthalocyanine monomer, 4,4'-bis (3,4-dicyanophenoxy) biphenyl (BPH), was synthesized in our laboratory. The synthetic procedure and characterization were reported previously [6]. 4,4'-Diaminediphenyl sulfone (DDS, as curing agent) was purchased from Sichuan Dongcai chemicals.

### Preparation of the BPH/CNTs masterbatch

The preparation process of the BPH/CNTs masterbatch was carried out as follows. First, BPH monomer (190 g) was melted at 250 °C in a beaker with a mechanical stirrer for 10 min. Then, CNTs (10 g) was added slowly but stirred vigorously for 15 min, producing a dark green BPH/CNTs mixture. Then the mixture was allowed to cool to room temperature, producing a dark green solid. Finally, the solid was smashed in a high-speed disintegrator for 5 min; the

BPH/CNTs masterbatch powder (CNTs content: 5 wt%) was thus obtained.

### Preparation of the Pc/CNTs nanocomposites

For a comparison, Pc/CNTs nanocomposite containing 2 wt% CNT content was prepared by direct melt-mixing. Firstly, BPH monomer (190 g) was melted at 250 °C in a beaker with a mechanical stirrer for 10 min. Then, DDS was added and kept for 5 min. Next, CNTs (10 g) were added slowly but stirred vigorously for 15 min, producing a dark green BPH/CNTs mixture. Finally, the mixture was poured into a preheated mold (250 °C) and cured by a sequential mode of temperature program at 250 °C, 280 °C, 300 °C, 350 °C, and 370 °C for 4 h, respectively. After being cured and cooled to room temperature, Pc/CNTs nanocomposite was finally obtained.

Pc/CNTs nanocomposites with different CNTs (0.5 wt%; 1 wt%; 2 wt%; 3 wt%; 5 wt%) loading were prepared by diluting 5 wt% BPH/CNTs masterbatch through adding weight-measured BPH. And the next procedures were carried out as identically as melt-mixing method described above.

### Characterizations

The morphology of the fracture surfaces of the Pc/CNTs nanocomposites was observed with scanning electron microscope (JEOL JSM-5900LV). Resistivity measurements were performed using the conventional four-probe method. Dielectric measurements for the Pc/CNTs nanocomposites were performed by using a dielectric analyzer (DEA 2970, TA Instruments) as reported before [23, 28]. Flexural tests (three-point bending mode, crosshead: 5 mm/min) of the samples were performed with a SANS CMT6104 series desktop electromechanical universal testing machine (Shenzhen, China) at room temperature. The final results were calculated as averages of five specimens for each Pc/CNTs nanocomposite. Thermogravimeric analysis (TGA) was carried out under both nitrogen and air atmosphere at a heating rate of 10 °C/min using TA Q50 series analyzer system combination with data processing station.

## Results and discussions

### Effect of blending method on the properties of Pc/CNTs nanocomposites

The 2 wt% CNTs-filled Pc nanocomposites were prepared by melt-mixing and masterbatch methods and their physical properties were summarized in Table 1. With the same CNTs content, Pc/CNTs nanocomposites prepared by

**Table 1** Electrical, dielectric, mechanical and thermal properties of 2 wt% CNTs-filled Pc nanocomposite prepared by Melt-mixing and Masterbatch methods

| Properties of 2 wt% CNT-filled Nanocomposite | | | Melt-mixing | Masterbatch |
|---|---|---|---|---|
| Electrical Property | Resistivity ( $10^7$ Ω cm) | | 0.90 | 1.37 |
| Dielectric Property | Dielectric Constant | 0.1 kHz | 16.18 | 66.52 |
| | | 100 kHz | 9.16 | 17.62 |
| | Dielectric Loss | 0.1 kHz | 0.43 | 0.94 |
| | | 100 kHz | 0.07 | 0.20 |
| Mechanical Property | Flexural Modulus (MPa) | | 4076.82 | 3977.2 |
| | Flexural Strength (MPa) | | 85.32 | 109.38 |
| Thermal Property | $T_{5\%}$ (°C) | | 545.01 | 536.05 |
| | $T_{10\%}$ (°C) | | 590.08 | 576.37 |
| | $T_{max}$ (°C) | | 557.34 | 545.43 |

masterbatch method show better dielectric and mechanical properties than those prepared by direct melt-mixing method. For example, dielectric constants of Pc/CNTs nanocomposites prepared by masterbatch method are 2–4 times larger than those of samples prepared by melt-mixing method. The flexural strength of Pc/CNTs nanocomposites prepared by masterbatch is also 24.06 MPa higher than those of Pc/CNTs nanocomposites prepared by melt-mixing. The difference of dielectric and mechanical properties can reflect the different dispersion and adhesion state of CNTs in those two systems, which is confirmed by their SEM images. It can be seen in Fig. 1(a) and (b) that CNTs in melt-mixing systems aggregate heavily with sword-like bundles or entanglements; and many CNTs are pulled-out with sharp ends. However, CNTs in the masterbatch system exhibit relatively better distributions and most of CNTs are broken rather than pulled out from the matrix. As a result, better dispersion and adhesion of masterbatch contribute more to dielectric and mechanical performances of resulted nanocomposites. It is also interesting to note that Pc/CNTs nanocomposites prepared by direct melt-mixing method show higher thermal stabilities than those by masterbatch method. Wu et al. [9] reported no obvious thermal increments in the polylactide/CNT composites and the authors attributed those to the crosslinking reduction of polycarbonate at the presence of CNTs and the additional components or impurities such as compatibilizer or remaining catalyst from the CNT synthesis. This explanation may be true to BPH/CNTs composites since well-dispersed CNTs may retard the curing degree of BPH matrix itself and CNTs were not chemically treated in this study. Schartel et al. [10] even observed a remarkable decrease in the polycarbonate/CNT composites and the authors thought bare and aggregated CNTs could take up heat and obstruct transport of degradation products more effectively. In this sense, these results also manifest that the dispersion states of CNTs in the masterbatch are better than those in the direct melt-mixing, which agrees well with the SEM observations. Therefore, in the following study, masterbatch method was chosen to prepare Pc/CNTs nanocomposites
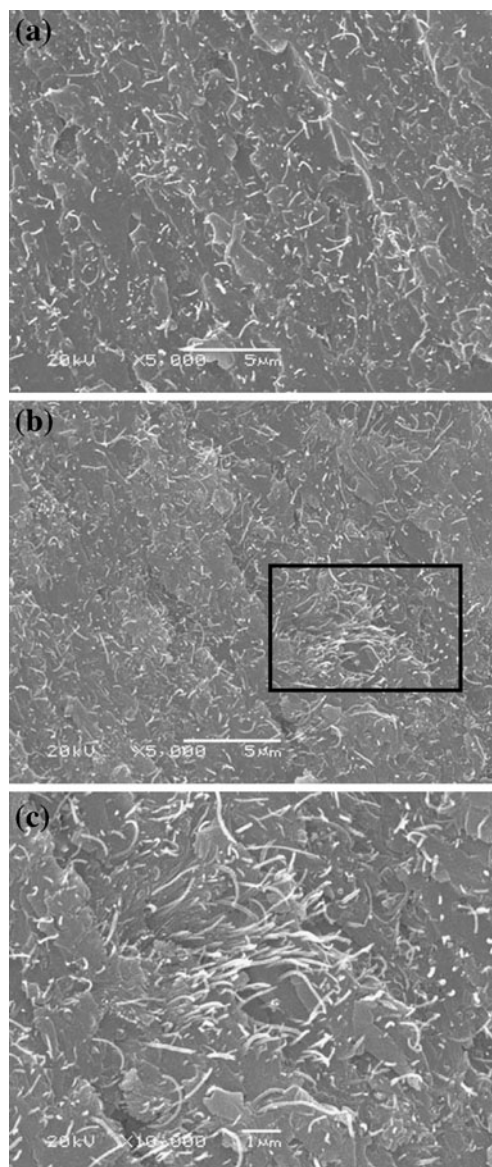


**Fig. 1** SEM images of 2 wt% CNTs-filled Pc nanocomposites prepared by **a** masterbatch method, **b** melt-mixing method and **c** enlarged black area of **b**

and their physical properties as a function of CNTs loading were investigated.

## Electrical and dielectric properties of Pc/CNTs nanocomposites

Figure 2 is a plot of the electrical resistance versus CNT loading of the Pc/CNTs nanocomposites measured at room temperature. The electrical resistance decreases with the increase in the amount of the CNT loading in the nanocomposites. A sharp decrease of the electrical resistance was observed between 0.5 and 1 wt%. When the weight percentage of the CNTs increased to 1 wt%, electrical resistance of the nanocomposite dramatically decreased, being 3 orders of magnitude smaller than that of the pure Pc matrix. This may be ascribed primarily to the large aspect ratio of the conductive CNTs. Similar electrical behavior was also reported in other CNTs-based nanocomposites and this can be attributed to the fact that a percolation network of CNTs was formed within the composite systems [24–27]. In our case, the decrease in the electrical resistance is still not large. This may be due to that thermoset BPH monomer itself can be cured and net-like macromolecules were formed after heat treatment while good thermal conductivities of CNTs may further promote BPH curing process. As a result, CNTs or CNTs network is inevitably separated by the polymer chains, leading to small decrease of electrical resistance values.

Figure 3 shows the dielectric constant of Pc/CNTs nanocomposite as a function of CNT loading at 100 Hz. It can be seen that dielectric constant of 0.5 wt% CNTs-filled Pc nanocomposite almost shows the similar value
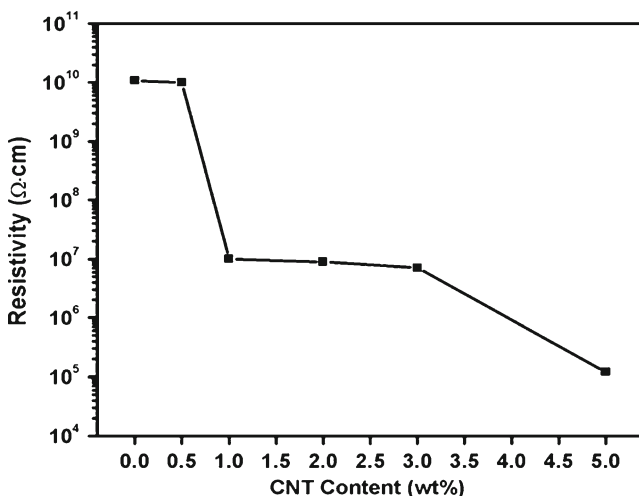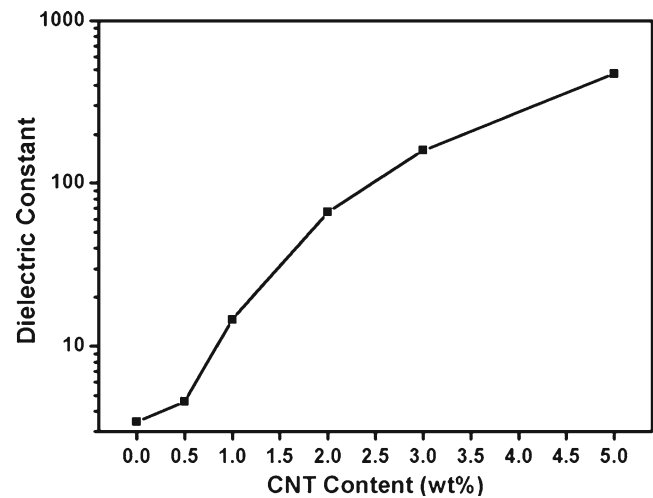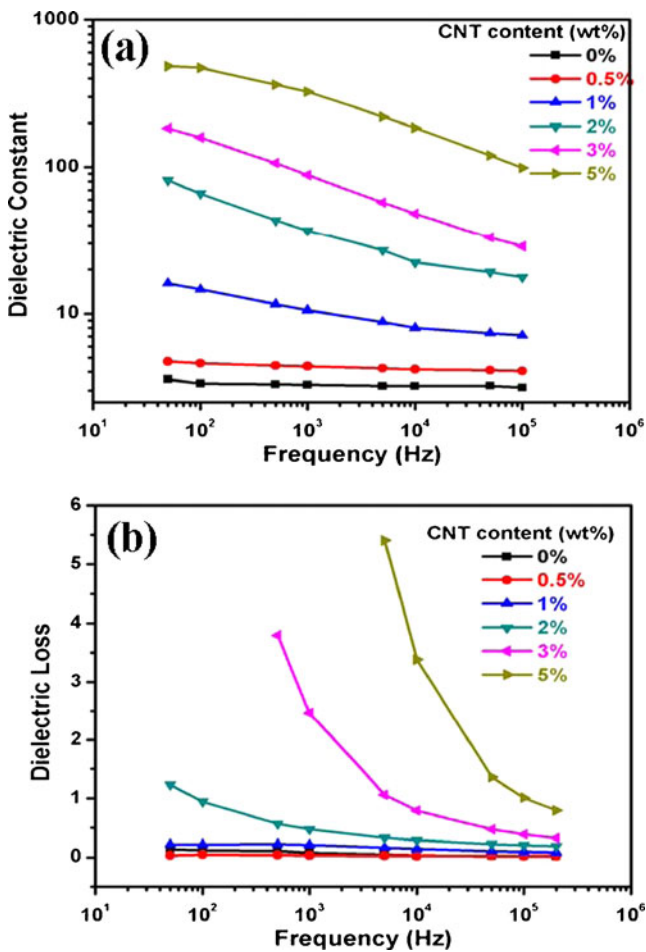
**Fig. 3** Dielectric constant of Pc/CNTs nanocomposite as a function of CNT content at 100 Hz

as that of Pc matrix. However, incorporation of 1 wt% CNTs significantly increases the dielectric constant, from 3.44 to 14.57, leading to 320 % increment. The dramatic increase at 1 wt% is a critical transition for dielectric constant, which agrees well with the electrical resistance observation. From that point on, dielectric constant of Pc/CNTs nanocomposite increases steadily as CNT content goes. For 5 wt% CNTs-filled Pc nano-composite, a high dielectric constant of 472.72 is obtained. The increase in the dielectric constant can be attributed to polarization effect among the high aspect ratio CNTs [23]. In this system, many conducting CNTs are isolated by thin dielectric layers; the high dielectric constant values originate in the significant blocking of charge carriers at internal interfaces (namely the MWS effect) under an electric field, because of the formation of a large number of micro-capacitors [25].

The dielectric transition at 1 wt% CNTs loading can be also confirmed by their frequency dependence. Figure 4 shows the dielectric constant and loss of the Pc/CNTs nanocomposites as a function of frequency for different CNT contents at room temperature. Consequently, dielectric constant increase with the increasing CNT content at the specified frequency. However, the dependence of dielectric constant on the frequency is distinguished with different CNT content. Namely, below the 1 wt% CNTs content, the dielectric constant and loss of Pc/CNTs nanocomposites show little frequency dependence. However, when CNT loading exceeds 1 wt%, the dielectric relaxation becomes evident, which results in a decrease of the dielectric constant. These results are consistent with the observations in Figs. 2 and 3. To conclude, the dramatic electrical and dielectric transition happens when CNT content is about 1 wt%.
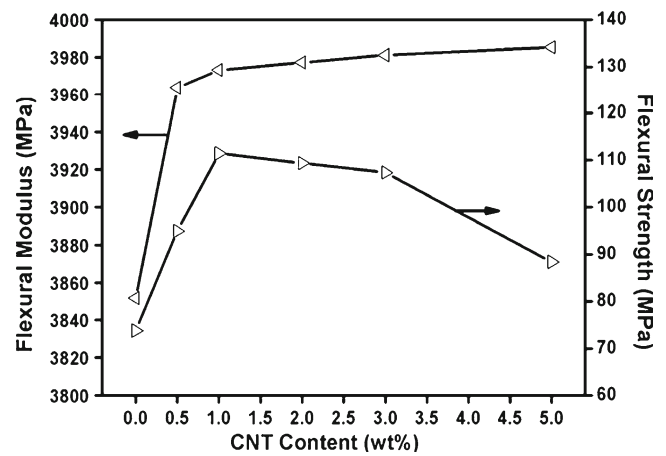
**Fig. 2** Resistivity of Pc/CNTs nanocomposite as a function of CNT content

**Fig. 4** Dielectric properties of Pc/CNTs nanocomposite as a function of frequency: **a** dielectric constant and **b** dielectric loss.



**Fig. 5** Mechanical properties of Pc/CNT nanocomposite as a function of CNT content: flexural modulus and flexural strength.

Mechanical and morphological properties of Pc/CNTs nanocomposites

The flexural test can measure the deformation energy or fracture strength that bears the bending moment for the tested materials. Figure 5 shows the effect of CNT content on the flexural properties of Pc/CNTs nanocomposites. It can be seen that the increase in the flexural modulus is very encouraging with small CNT addition. For example, flexural modulus shows an increase from 3852 MPa in the Pc matrix to 3964 MPa in the 0.5 wt% CNTs-filled Pc nanocomposite.

Figure 5 also depicts the flexural strength of Pc/CNTs nanocomposites. As CNT content increases, the flexural strength of the Pc/CNTs nanocomposite increases firstly, and then becomes stable, and decrease afterwards. It is interesting to note that the maximized flexural strength of 111.4 MPa is obtained in the 1 wt% CNTs-filled Pc nanocomposite, which is increased by 51.4 % in comparison with Pc host (73.7 MPa). And then with higher CNT loading (1–3 wt%), the flexural strength of the nanocomposites slightly decrease. These mechanical improvements can

be due to the fact that uniform-dispersed CNTs restrict the mobility of polymer chains of Pc, while the processing method of masterbatch can promote compatibility and adhesion between CNTs and Pc matrices. High strength and aspect ratio of CNTs also contributes to the mechanical improvement. Moreover, a gradual formation of CNT network can further restrict polymer chain and result in the optical mechanical performances. Comprehensively evaluating, Pc/CNTs nanocomposites with 1–3 wt% CNT content showed the best mechanical performances. However, the decrease of flexural strength in the 5 wt% CNTs-filled nanocomposite can be due to the aggregate of CNTs and also the decreased curing degree of Pc in the presence of aggregated CNTs.

Mechanical properties of the nanofiller/polymer system are related to the dispersion, orientation, adhesion, interfacial interaction and stabilization of the nanofillers in/with the polymer matrices [13, 18, 28]. Hence, fracture surface images of the nanocomposite are given to further evaluate their mechanical properties, as is shown in Fig. 6. The surface of neat Pc host is quite smooth, showing a typical brittle fracture (Fig. 6a). However, incorporation of CNTs significantly changes the surface of Pc (Fig. 6b-c), increasing the surface area on the fracture surface. From the Fig. 6b-c, it can be also observed CNTs are uniformly dispersed in both 1 and 3 wt% CNTs-filled Pc nanocomposites. In addition, pull-out phenomena can been observed in the nanocomposites, but most of CNTs are well embedded in the Pc matrix, indicating that CNTs have good adhesion to Pc host due to merits of the masterbatch processing method. These results confirmed the enhancement of the mechanical performances investigated, especially for 1–3 wt% CNTs-filled Pc nanocomposites.
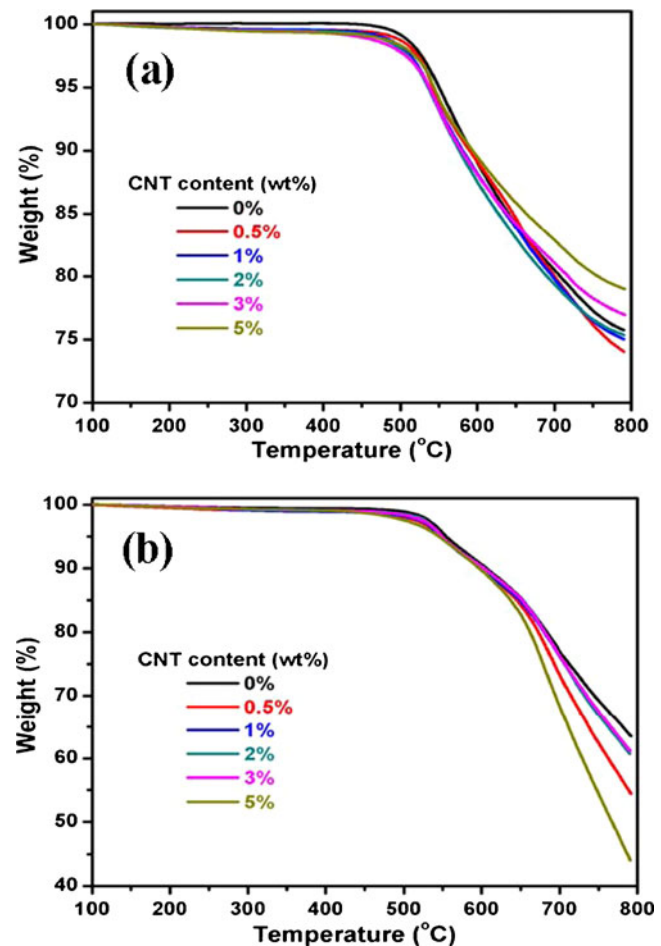
Thermal stabilities of Pc/CNTs nanocomposites

To show the effect of CNTs on the thermal properties of Pc composites, the main TGA results (Fig. 7) performed in

both nitrogen and air atmosphere were summarized in Table 2, in which the initial decomposition temperatures at weight loss of 5 %, 10 %, 30 % ($T_{d5\%}$, $T_{d10\%}$, $T_{d30\%}$) and maximal decomposition temperature ($T_{max}$) were displayed. For the $T_{d5\%}$, $T_{d10\%}$, $T_{d30\%}$ and $T_{max}$, they are all higher than 535 °C, indicating the excellent thermal and thermo-oxidative stabilities of Pc/CNTs nanocomposites. Compared with Pc matrix, however, no improvement in thermal and thermo-oxidative stabilities was observed in the composites. Wu et al. [9] reported no obvious thermal increments in the polylactide/CNTs nanocomposites and Schartel et al. [10, 29] also observed a remarkable decrease in the polycarbonate/CNTs composites.
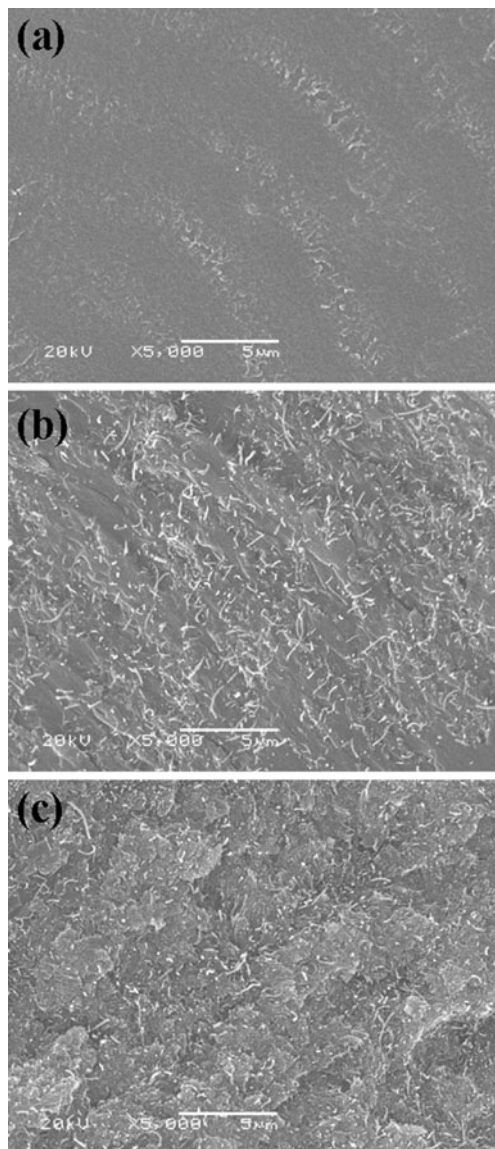


Fig. 6 SEM images of fractured surface of the Pc/CNTs nanocomposites containing: **a** 0 wt% CNT (neat Pc matrix), **b** 1 wt% CNT, and **c** 3 wt% CNT



Fig. 7 Thermal stabilities of Pc/CNTs nanocomposites at different atmosphere: **a** nitrogen and **b** air

## Conclusions

To prepare good Pc/CNTs nanocomposites, the effect of different blending method melt-mixing and masterbatch were firstly studied. Consequently, CNTs in melt-mixing systems aggregate heavily with sword-like bundles or entanglements; and many CNTs are pulled-out with sharp ends.

Table 2 Thermal stabilities of Pc/CNTs nanocomposites under nitrogen and air atmosphere

| CNT Content (wt %) | In Nitrogen | | | In Air | | |
|---|---|---|---|---|---|---|
| | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{max}$ (°C) | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{max}$ (°C) |
| 0 | 550.2 | 591.57 | 556.59 | 554.80 | 606.01 | 547.29 |
| 0.5 | 542.22 | 589.79 | 538.92 | 548.42 | 598.32 | 550.43 |
| 1 | 537.34 | 580.96 | 540.78 | 547.06 | 598.54 | 538.92 |
| 2 | 536.05 | 576.37 | 545.43 | 548.60 | 600.97 | 538.92 |
| 3 | 537.54 | 579.28 | 545.43 | 549.08 | 602.76 | 545.43 |
| 5 | 543.5 | 593.7 | 541.71 | 545.07 | 596.76 | 553.50 |

Masterbatch nanocomposites had good CNT dispersion state and more obviously enhanced physical properties. Then, Pc/CNTs nanocomposites containing different CNT content were prepared by masterbatch route; and the feasibility of using Pc/CNTs nanocomposites was investigated by evaluating their electrical, dielectric, mechanical, morphological and thermal properties as a function of CNT loading. Consequently, the dramatic electrical and dielectric transition happened when CNTs was about 1 wt%. For the 1 wt% CNTs-filled Pc nanocomposites, a 51.4 % increase in flexural strength was obtained and flexural modulus was also improved from 3851.7 MPa to 3973.3 MPa. These improvements were mainly due to the fact that masterbatch method can promote good dispersion and strong adhesion of CNTs in/to the Pc host. All Pc/CNTs nanocomposites showed high thermal and thermo-oxidative stabilities up to 535 °C. Pc/CNTs nanocomposites with multifunctional properties can find uses under some critical circumstances with requirements of high strength and temperatures.

In addition, large-scale production of CNTs using iron–Pc polymers as only carbon source at ambient pressure in nitrogen atmosphere has been reported in our lab [2]. However, the mechanism remained unclear. This work investigates the presence of CNTs on the properties of Pc polymers and may provide us some useful information on discovering the mechanism behind the production of CNTs from iron–Pc polymer.

# References

1. Warzel ML, Keller TM (1993) Tensile and fracture properties of a phthalonitrile polymer. Polymer 34:663–666
2. Lei YJ, Zhao R, Zhan YQ, Meng FB, Zhong JC, Yang XL, Liu XB (2010) Generation of multiwalled carbon nanotubess from iron–phthalocyanine polymer and their novel dielectric properties. Chem Phys Lett 496:139–142
3. Keller TM (1988) High-performance, electrically conductive polymers. Chemtech 18:635–639
4. Giuliani JF, Keller TM (1989) Phthalonitrile conductive polymer chemica vapor sensors. Sens Mater 1:247–253
5. Sastri SB, Armistead JP, Keller TM (1996) Phthalonitrile-carbon fiber composites. Polym Compos 17:816–822
6. Yang XL, Lei YJ, Zhong JC, Zhao R, Liu XB (2011) Preparation and thermal properties of novel phthalonitrile oligomer containing biphenyl ethernitrile/bisphthalonitrile blends. J Appl Polym Sci 119:882–887
7. Du RH, Li WT, Liu XB (2009) Synthesis and thermal properties of bisphthalonitriles containing aromatic ether nitrile linkages. Polym Degrad Stabil 94:2178–2183
8. Brunovska Z, Lyon R, Ishida H (2000) Thermal properties of phthalonitrile functional polybenzoxazines. Therm Acta 357:195–203
9. Wu DF, Wu L, Zhang M, Zhao YL (2008) Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes. Polym Degrad Stabil 93:1577–1584
10. Schartel B, Potschke P, Knoll U, Abdel-Goad M (2005) Fire behaviour of polyamide 6/multiwall carbon nanotubes nanocomposites. Eur Polym J 41:1061–1070
11. Zhan YQ, Meng FB, Yang XL, Lei YJ, Zhao R, Liu XB (2011) Synthesis, characterization and properties of multifunctional poly (arylene ether nitriles) (PEN)/CNTs/Fe$_3$O$_4$ nanocomposites. J Polym Sci, Part B: Polym Phys 49:611–619
12. Du JH, Bai J, Cheng HM (2007) The present status and key problems of carbon nanotubes based polymer composites. Express Polymer Lett 1:253–273
13. Prashantha K, Soulestin J, Lacrampe MF, Claes M, Dupin G, Krawczak P (2008) Multi-walled carbon nanotubes filled polypropylene nanocomposites based on masterbatch route: Improvement of dispersion and mechanical properties through PP-g-MA addition. Express Polymer Lett 10:735–745
14. Sun J, Gao L (2003) Development of a dispersion process for carbon nanotubess in ceramic matrix by heterocoagulation. Carbon 41:1063–1068
15. Mukherjee M, Bose S, Nayak GC, Das CK (2010) A study on the properties of PC/LCP/MWCNT with and without compatibilizers. J Polym Res 17:265–272
16. Kuilla T, Bhadra S, Yao DH, Kim NH, Bose S, Lee JH (2010) Recent advances in graphene based polymer composites. Prog Polym Sci 35:1350–1375
17. Zhan YQ, Yang XL, Meng FB, Lei YJ, Zhong JC, Zhao R, Liu XB (2011) Viscoelasticity and thermal stability of poly(arylene ether nitrile) nanocomposites with various functionalized carbon nanotubes. Polymer Int 60:1342–1348
18. Sahoo NG, Rana S, Cho JW, Li L, Chan SH (2010) Polymer nanocomposites based on functionalized carbon nanotubes. Prog Polym Sci 35:837–867
19. Du JH, Zhao L, Zeng Y, Zhang LL, Li F, Liu PF, Liu C (2011) Electrical conductivity of carbon nanotubes/poly (vinylidene fluoride) composites prepared by high-speed mechanical mixing. Carbon 49:1094–1100
20. Masuda J, Torkelson JM (2008) Dispersion and major property enhancements in polymer/multiwall carbon nanotubes nanocomposites via solid-state shear pulverization followed by melt mixing. Macromolecules 41:5974–5977
21. Pegel S, Pötschke P, Petzold G, Alig I, Dudkin SM, Lellinger D (2008) Dispersion, agglomeration, and network formation of multiwalled carbon nanotubess in polycarbonate melts. Polymer 49:974–984
22. Pötschke P, Bhattacharyya AR, Janke A, Goering H (2003) Melt mixing of polycarbonate/multi-wall carbon nanotubes composites. Compos Interfac 10:389–404
23. Luechinger NA, Booth N, Heness G, Bandyopadhyay S, Grass RN, Stark WJ (2008) Surfactant-free, melt-processable metal–polymer hybrid materials: use of graphene as a dispersing agent. Adv Mater 20:3044–3049
24. Ahmad K, Pan W, Shi SL (2006) Electrical conductivity and dielectric properties of multiwalled carbon nanotubes and alumina composites. Appl Phys Lett 89:1331221–1331223
25. Yang YL, Gupta MC, Dudley KL, Lawrence RW (2004) The fabrication and electrical properties of carbon nanofibre–polystyrene composites. Nanotechnology 15:1545–1548
26. Gojny FH, Wichmann MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, Schulte K (2006) Evaluation and identification of

electrical and thermal conduction mechanisms in carbon nanotubes/epoxy composites. Polymer 47:2036–2045

27. El Shafee E, El Gamal M, Isa M (2012) Electrical properties of multi walled carbon nanotubess/poly(vinylidenefluoride/trifluoroethylene) nanocomposites. J Polym Res 19:9805–9813

28. Yang XL, Zhan YQ, Yang J, Zhong JC, Zhao R, Liu XB (2012) Synergetic effect of cyanogen functionalized carbon nanotubes and graphene on the mechanical and thermal properties of poly (arylene ether nitrile). J Polym Res 19:9806–9812

29. Schartel B, Braun U, Knoll U, Bartholmai M, Goering H, Neubert D, Pötschke P (2008) Mechanical, thermal, and fire behavior of bisphenol A polycarbonate/multi-wall carbon nanotubes nanocomposites. Polymer Eng Sci 48:149–158