

A nanotube colorant for synthetic fibers with much improved properties†

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Carbon nanotubes have for the first time been demonstrated as a novel and effective colorant for synthetic fibers such as poly(*p*-phenylene terephthalamide). Compared with the conventional carbon black, the nanotube colorant was found to be more uniformly dispersed in the polymer matrix with a better coloration effect and higher coloration stability. The nanotube colorant also enabled much improved electrical, mechanical, and thermal properties compared with the pure polymer and carbon black-colored polymer fibers.

Introduction

The coloration of various materials is an ancient technology. It was reported that the ancient Chinese had already mastered the coloration technology for the cotton fiber five thousand years ago. This technology had been further widely used for synthetic fibers upon their discovery more than a century ago.^{1,2} In the case of a black color, carbon black has been used in the particular case of mass coloration where the colorant is extruded in the polymer melt.^{3–6} However, it remains challenging to further improve the coloration effect as the carbon black particles are weakly attached on synthetic fibers, which in fact also decreases their stability as they may be easily detached during the use. In addition, it is difficult to modify the carbon black to meet the different requirements from various fiber materials. For instance, poly(*p*-phenylene terephthalamide) (PPTA) represents a high-performance synthetic fiber for many structural materials, but it remains very difficult to dye PPTA by carbon black with high efficiency.^{7–10} Therefore, it is still required to improve the coloration stability and other physical properties of the PPTA fiber by introducing new colorants.

On the other hand, due to the unique structure and excellent electrical, mechanical, and thermal properties, carbon nanotubes (CNTs) have been widely studied as an effective additive for a broad spectrum of materials, particularly, synthetic polymers.^{11–16} For instance, CNTs have a high electrical conductivity at the level of 10^5 S cm^{-1} , and they were incorporated into polymers to realize a conductive property or to improve the electronic property.^{17–20} As another example, CNTs are the strongest material ever discovered by the human kind, and they were introduced to enhance the mechanical property of

polymers.^{21–25} In order to further improve the property of composite materials, CNTs can also be easily modified with functional groups to interact with the designed polymer molecules.^{26,27} Due to the introduction of CNTs at the nanoscale, the resulting nanocomposite materials could fully take advantage of the excellent physical properties of CNTs. As CNTs have also been realized to be produced at large scale with low cost, they can be widely used as a functional moiety in the synthesis of high-performance materials.^{28,29} However, to the best of our knowledge, no reports are available for the use of CNTs as colorant materials.

Herein, we have first demonstrated that CNTs can be used as a novel and effective colorant for synthetic fibers. PPTA is carefully investigated as a synthetic fiber model, and it can be uniformly colorized with multi-walled carbon nanotubes (MWCNTs). The microscopy technology revealed a uniform distribution of MWCNTs in the polymer matrix with good structural stability. A lower content of MWCNTs exhibited a better coloration effect on the PPTA than the conventional carbon black. In addition, the colorized PPTA with MWCNTs showed much improved electrical, mechanical, and thermal properties compared with the pure PPTA and conventionally colorized PPTA with carbon black.

Experimental section

Poly(*p*-phenylene terephthalamide) (PPTA) powder was provided by Yantai Tayho Advanced Materials and used as received. Sulfuric acid (98%) was obtained from Sino-pharm Chemical Reagent Co., Ltd. MWCNTs were ordered from Shenzhen Nanotech Port and Beijing Nachen S&T. Scotch Magic Tape with a thickness of 50 μm was obtained from 3 M. The spherical particles of carbon black were contributed by Yantai Tayho Advanced Materials with diameters of 20–30 nm.

In the fabrication of MWCNT-colored PPTA materials, a stable MWCNT suspension (6–150 mg) in sulfuric acid (98% H_2SO_4 , 10 g) was firstly prepared after ultrasonic treatment for 30 min, followed by addition of the PPTA powder (600 mg) and

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mechanical stirring with a speed of 500 revolutions per minute for 30 min. The mixture was coated into stripes on the glass slide with the thickness of 50, 100, and 150 μm through a doctor-blading shaping method. The resulting stripes were finally treated by a coagulating bath with the de-ionized water (pH of 7). The strip sizes were measured by scanning electron microscopy (SEM).

The color-fastness measurements were made in a 1 mol L⁻¹ NaOH aqueous solution. Both carbon black-colored and MWCNT-colored PPTA materials were directly dropped into the alkali solution, and the solution temperature was maintained at 25 °C. After two weeks, the samples were taken out of the alkali solution and washed by the de-ionized water. They were characterized by optical microscopy after drying for 30 min at 60 °C.

The structure was characterized by SEM (Hitachi, FE-SEM S-4800 operated at 1 kV) and optical microscopy (Olympus, BX51). The thermogravimetric analysis was conducted on Shimadzu DTG-60H by heating the sample from room temperature to 800 °C with a rate of 10 °C min⁻¹ in air. Fourier transform infrared spectroscopy characterization was made using a Shimadzu IRPrestige-21. Raman measurements were performed on a Renishaw inVia Reflex with an excitation wavelength of 514.5 nm and a laser power of 20 mW at room temperature. Mechanical tests were performed on HY-0350X from Shanghai Heng Yi Precision Instrument. The electrical resistance was measured by a typical two-probe method with Maynuo M8813 as a current or voltage source.

Results and discussion

In the preparation of the CNT/polymer composite materials, a solution or melting process had been generally used with low cost and high efficiency.^{30,31} Here the MWCNTs were introduced to the PPTA matrix through a simple solution process at room temperature. The experimental details are described in the experimental section, and the PPTA material in a strip format was mainly studied as an example. Here the diameter and length of the MWCNTs were ~ 10 nm and 10–20 μm unless specified. Fig. 1 compares the photographs of a pure PPTA strip, a PPTA strip colorized with MWCNTs (3% for the weight concentration), and a PPTA fiber colorized with carbon black (5% for the weight concentration). Obviously, the MWCNT showed a better coloration effect than the carbon black. Here the pure PPTA seems a little yellow in color. Fig. 2 further compares the colorized PPTA by using the conventional carbon black and MWCNTs under scanning electron microscopy (SEM). The top surface based on the MWCNT appears smoother than the carbon black. In addition, according to the cross-sectional SEM images, MWCNTs were more uniformly dispersed in the polymer matrix than the carbon black. The π - π interaction between the PPTA and MWCNT may explain the good distribution of MWCNTs in the PPTA matrix.^{8,10}

To verify the interaction between PPTA and MWCNT, Fourier transform infrared (FTIR) and Raman spectroscopy were used to investigate the MWCNT/PPTA nanocomposite. Fig. 3a and S1† have compared the FTIR spectra of the pure PPTA and MWCNT/PPTA composite. The characteristic peaks at 1515, 1409, and 1319 cm⁻¹ shift to 1512, 1406, and 1317 cm⁻¹, respectively, which indicates the interaction between PPTA and

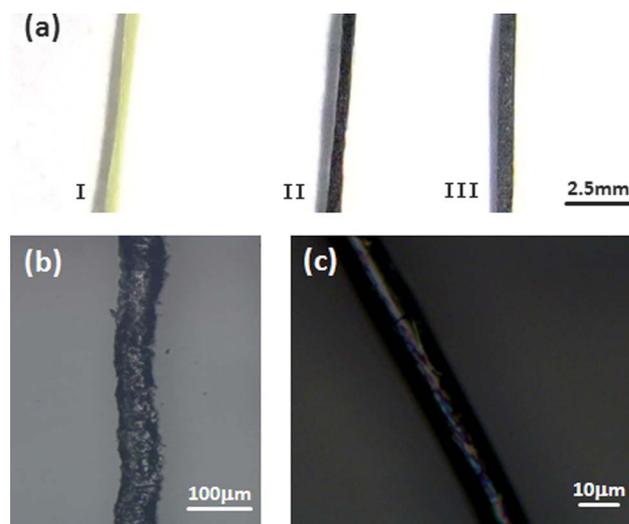


Fig. 1 (a) Photographs of pure PPTA strip (I), PPTA strip colorized with MWCNTs (II), and PPTA fiber colorized with the conventional carbon black (III). (b) Optical micrograph of a PPTA strip colorized with MWCNTs. (c) Optical micrograph of a PPTA fiber colorized with the conventional carbon black.

MWCNT.^{32,33} Fig. 3b further compares Raman spectra of MWCNTs before and after incorporation into the PPTA. The G and D bands at 1569 and 1343 cm⁻¹ show obvious shifts to 1571 and 1345 cm⁻¹, respectively. These results clearly confirmed the strong π - π interaction between MWCNT and benzene unit in the PPTA.^{10,32}

The above interaction between MWCNT and PPTA enables the high coloration stability. A comparison study had been made for the PPTA material colorized by carbon black and MWCNT after treatments by NaOH aqueous solution (concentration of 1 mol L⁻¹) for two weeks (Fig. 4). Obviously, the PPTA strip colorized by MWCNTs well maintained the original black color,

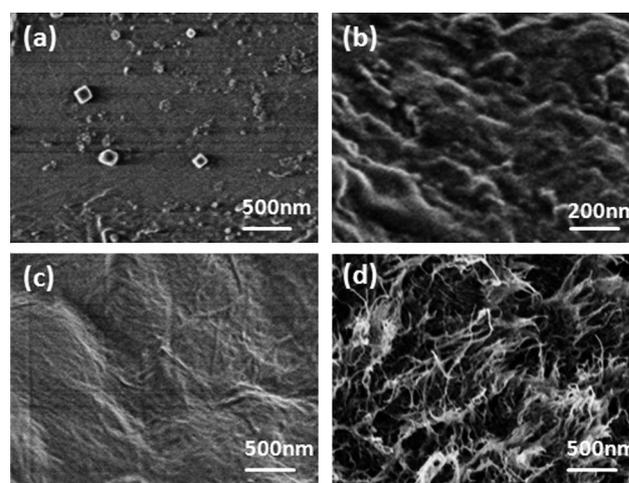


Fig. 2 Comparison of the PPTA material colorized with the carbon black and MWCNTs by scanning electron microscopy (SEM). (a) Top and (b) cross-sectional images of a PPTA fiber colorized with the carbon black, respectively. (c) Top and (d) cross-sectional images of a PPTA strip colorized with MWCNTs, respectively.

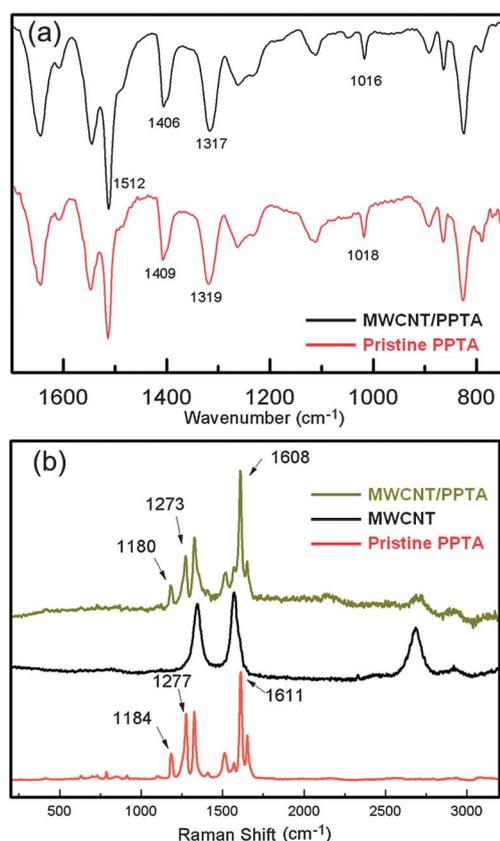


Fig. 3 (a) FTIR spectra of pristine PPTA and 5% MWCNT-colored PPTA. (b) Raman spectra of pristine PPTA, MWCNT, and 5% MWCNT-colored PPTA.

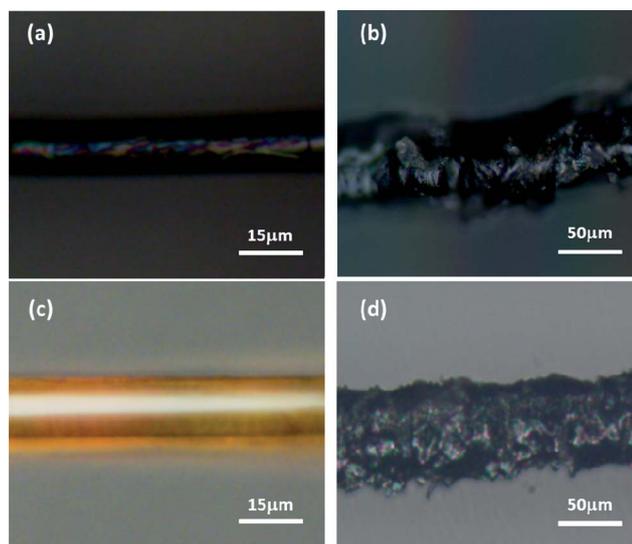


Fig. 4 Characterization of the coloration stability by optical microscopy. The PPTA material colored by (a) carbon black and (b) MWCNTs. (c) and (d) Alkaline treatments of (a) and (b) for 2 weeks, respectively.

while the PPTA fiber colored by black carbon severely faded and appeared yellow, which belonged to the pure PPTA. The coloration difference was further confirmed by the structure

characterization under SEM (Fig. S2†). For the MWCNT-colored PPTA strip, the well dispersed nanostructure of MWCNTs in the PPTA matrix remained almost unchanged. As a strong contrast, almost no carbon black particles were found in the PPTA matrix, and the colorized structure had been in fact desorbed into the aqueous alkali solution. The removal of carbon black from PPTA can be explained by the following fact. Firstly, as previously discussed, the particles of carbon black had been physically attached onto the smooth outer surface of PPTA fibers, and the interaction between carbon black and PPTA was relatively weak. Secondly, the carbon black particles were generally modified with functional groups such as carboxyl groups on the surface to improve the coloration, and they could react with the alkaline. Therefore, the carbon black particles were detached from the PPTA fiber during the alkaline treatment.

Pure PPTA is not electrically conductive. With the addition of MWCNTs, the resulting PPTA showed a dramatic increase in electrical conductivity with the increase of added MWCNTs. The conductivity was enhanced from less than 10^{-7} to 4 S cm^{-1} when the MWCNT weight concentration was increased from 3 to 28% (Fig. 5a). The main increase occurred at the concentration of less than 10%.

Besides the MWCNT concentration, the aspect ratio of MWCNTs played another critical role in the conductivity of

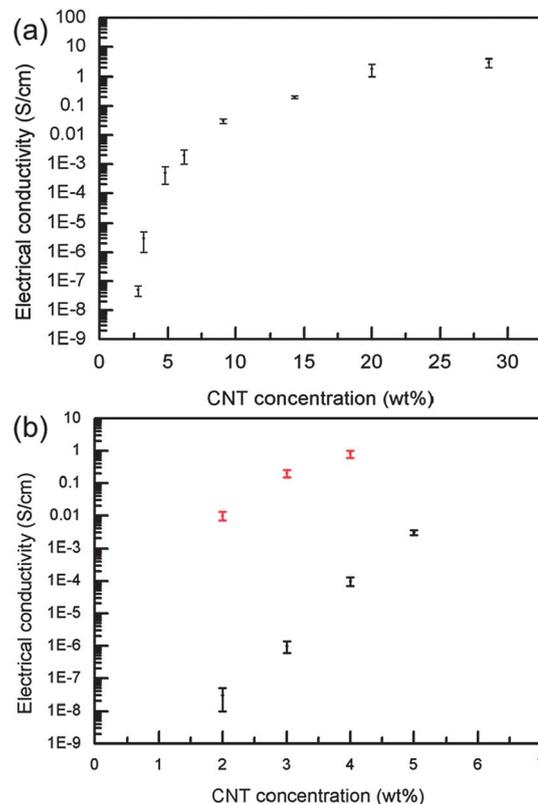


Fig. 5 (a) Dependence of the electrical conductivity of the colored PPTA on the concentration of MWCNTs with a length of $1 \mu\text{m}$ and diameter of $\sim 20 \text{ nm}$. (b) Comparison of the electrical conductivity of the colored PPTA in which MWCNTs show lengths of 1 (black color) and 100 (red color) μm with the same diameter of $\sim 20 \text{ nm}$.

colored PPTA. The electrical resistance of a MWCNT/polymer composite generally includes two parts, *i.e.*, the contact resistance among MWCNTs and the resistance of individual MWCNTs. As individual MWCNTs have very low electrical resistivity at the level of $10^{-5} \Omega \text{ cm}^{-1}$, the resistance in the colored PPTA is mainly determined by the contact resistance. In other words, the lengths of MWCNTs are critical to the improved degree of electrical conductivity in case that their diameters are the same. The longer the MWCNTs, the lower the number of contact points among the MWCNTs. Therefore, longer MWCNTs can dramatically increase the electrical conductivity. Fig. 5b compares the MWCNTs with the two different lengths of 1 and 100 μm . For a low MWCNT concentration of 2%, the conductivity based on the length of 100 μm is almost six orders of that based on the length of 1 μm . With the increase of MWCNT concentrations for the above two MWCNT samples, the improved degree derived from longer MWCNTs decreases, *e.g.*, ~ 5 orders at 3% and ~ 4 orders at 4%. This difference has not been previously discovered.

The effect of CNTs on the mechanical property of PPTA was also investigated by comparing the tensile strength and elastic modulus. Fig. 6a shows that, with the increasing MWCNT concentration from 0 to 3%, both tensile strength and elastic modulus were continuously and largely improved by about 57% and 87%, respectively. With the further increase of MWCNT concentration to 5%, the tensile strength was relatively slowly decreased by 9%, while the elastic modulus was decreased by 38%. Obviously, an optimal concentration was found for both

tensile strength and elastic modulus. In addition, the MWCNT concentration has a greater effect on the elastic modulus than the tensile strength. We also investigated the effect of the aspect ratio of MWCNTs on the mechanical property of the colored PPTA. As shown in Fig. 6b, the tensile strength slightly increases with the increasing aspect ratio from 200 to 2000 and then decreases with the further increase of aspect ratio. There were two reverse parameters which may affect the tensile strength of the PPTA composites. Generally, a higher aspect ratio enhances the interaction among MWCNTs and between MWCNT and PPTA, which produces an increase in the tensile strength. However, with the increase of aspect ratios, MWCNTs are more difficult to be well dispersed, and the MWCNTs are more easily aggregated to form relatively less uniform structures during the preparation of composite materials. The first parameter exceeds the second one at an aspect ratio below 1000, while the second parameter exceeds the first one at a higher aspect ratio. Differently, the elastic modulus continuously increases with the increasing aspect ratio. Specifically, it was increased by 25% with the increase of aspect ratios from 200 to 2000 and then dramatically increased by 110% with the further increase to 15 000.

It should be mentioned that the mechanical improvements after addition of MWCNTs were slightly lower than some other reports where either single-walled CNTs or external forces were generally used.³⁴ The smaller diameters increased the entanglement of the CNTs, while the external forces, such as shearing forces, induced the alignment of the CNTs. Both of them further increased the tensile strength and elastic modulus of the composite materials.

CNTs had been also widely studied to improve the thermal stability of polymers.^{35–37} As expected, the addition of MWCNTs improved the decomposition temperature of the PPTA. Fig. 7 compares the thermogravimetric graphs for pristine PPTA, black carbon-colored PPTA, and MWCNT-colored PPTA with different MWCNT concentrations. The accelerating decomposition temperature of PPTA remained almost unchanged after

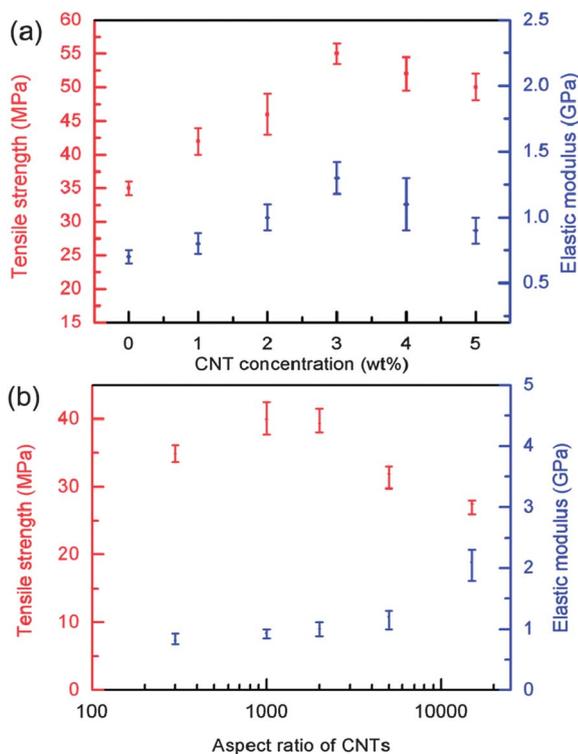


Fig. 6 (a) Dependence of the mechanical property of the colored PPTA on the MWCNT concentration. (b) Dependence of the mechanical property of the colored PPTA on the aspect ratio of MWCNTs with diameters of 10–20 nm.

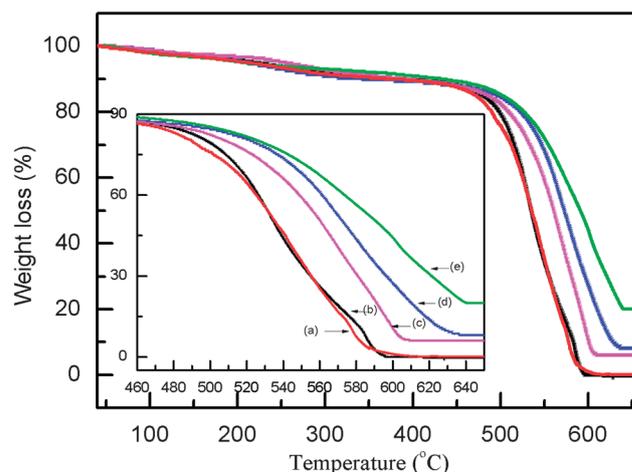


Fig. 7 Thermogravimetric analysis. (a) Pristine PPTA. (b) A PPTA fiber colored by carbon black with a weight concentration of 5%. (c) A PPTA strip colored by MWCNTs with a weight concentration of 1%. (d) A PPTA strip colored by MWCNTs with a weight concentration of 2%. (e) A PPTA strip colored by MWCNTs with a weight concentration of 10%.

colored by carbon black, while it had been greatly improved with the MWCNTs. The improved degree depended on the MWCNT concentration. For instance, the accelerating decompositions were increased from 538 for the pure PPTA to 568, 578, and 603 °C after addition of MWCNTs at concentrations of 1%, 2%, and 10%, respectively.

Conclusion

In summary, we have shown for the first time that MWCNTs can function as a novel colorant for the synthetic polymers. Due to the incorporation of the colorant at the nanoscale level and interaction between MWCNT and polymer, MWCNTs could be well distributed in the polymer matrix. Therefore, this nano-scaled colorant showed a much better coloration effect on the PPTA than the conventional carbon black. In addition, although no drawing processes which are generally used for the synthetic fiber were applied, the introduction of MWCNTs had already provided the PPTA strip with much increased electrical, mechanical, and thermal properties, which can be further greatly improved with the drawing treatment in the real application for PPTA fibers.¹⁹ The combined remarkable properties may enable a wide variety of promising applications, particularly, in the fields where good conductivity, high strength, and high thermal stability are required.

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