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The production of soft, durable, and electrically conductive polyester multifilament yarns by dye-printing them with carbon nanotubes

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Continuous yarns and/or fibers composed of carbon nanotubes (CNTs) are highly attractive due to their intrinsic ability to form a variety of macroscopic objects by simply knitting and/or weaving of the yarns/fibers. The production of continuous yarns of pure CNTs has been accomplished by “dry-spinning”, the mechanical process of spinning either the single-walled CNTs directly from a CVD (chemical vapor deposition) gaseous reaction zone [1, 2] or with the multi-walled CNTs previously grown as a vertically oriented CNT forest [3, 4] . In contrast, “wet-spinning”, the spinning of a “super-acid (100 + %sulfuric acid) suspension” [5] of the single-walled CNTs, produced purely CNT-based continuous fibers. The pure CNT-based yarns and/or fibers retained the advantageous properties of the individual nanotubes, such as the high electrical and thermal conductivities. However, the preparation of industrial quantities of the single-walled CNTs or the multi-walled CNT forests, the precursors for making the CNT-based yarns/fibers, is presently impractical.

Continuous fibers containing a few wt % of CNTs, obtained, for example, by incorporating the single-walled CNTs into PVA polymers [6, 7], have shown excellent fiber properties, but electrical and thermal conductivities were low because of limitations on the contents of CNTs. Despite the production of continuous fibers with up to 60 wt% CNT content [8], the development of the CNT-based continuous yarns/fibers having high industrial applicability remains a challenging issue.

In this study, we used CNTs as “dyestuffs” for producing CNT-based continuous yarns by directly dye-printing of polyester multifilament continuous yarns. To our best knowledge, this is the first use CNTs for direct dye-printing of continuous multifilament yarns. CNTs, even the multi-walled types, are characterized by extremely large aspect ratios, because of their nanometer sized diameters and their micrometer (~ few hundred micrometers) sized length. This so-called one-dimensional morphology of CNTs results in stronger adhesion properties (in comparison with the so-called zero-dimensional materials, such as carbon blacks), suggesting a possible application for directly employing CNTs as dyestuffs for dyeing of fibers, yarns, and textiles. Such application, as demonstrated in this study, was achieved by using CNTs at molecular levels (or tubular levels) for dispersions as dyestuffs. Typical CVD products of multi-walled CNTs (Baytubes® C 150P), received as powders, have been used for preparing the CNT-based dyestuffs. Briefly, 300 g of the CNT powders were introduced into 10 L of an aqueous solution containing 40 g of 3-(*N*,*N*-dimethylmyristylammonio)-propanesulfonate and 30 g of polyoxyethylene lauryl ether sulfonate, to prepare the raw CNT-suspension. This suspension was then used as the precursor for preparing the CNT-based dyestuffs by dispersing the CNT-aggregates at the molecular level using a continuously operating bead-mill system. Three essential strategies are involved in the preparation of the CNTs-based dyestuffs. i) Wetting of CNTs: air and moisture were displaced from the surfaces of the CNT-aggregates by replacing them with the dispersants. This objective was accomplished in the process of preparing the raw CNT-suspensions and the best wetting efficiencies were obtained by using a combination of 3-(*N*,*N*-dimethylmyristylammonio)-propanesulfonate, a zwitterionic type of surfactants and polyoxyethylene lauryl ether sulfonate, an anionic type of surfactant, as the dispersants. ii) Grinding of the “wetted CNT-aggregates”: CNT-aggregates, after being well wetted by the blended zwitterionic/anionic dispersants, were easily dispersed into individual tubes by very mild mechanical shear forces through the use of a continuously operating bead-mill system. (Hereafter, CNT-aggregates, after being dispersed into individual tubes, will be referred as the “molecular level (or tubular level) of dispersion”.) Particle size distributions, as measured using a dynamic light scattering size distribution analyzer (Fig. 1), showed that 95% of the overall particles exhibited mean diameters smaller than 270 nm, suggesting that most of the dispersion of CNTs in the CNT-based dyestuffs occurred at the molecular level. iii) Addition of a small amount of polymers into the dyestuffs: the electric resistivity of the CNT-dyed yarns can be precisely controlled at certain levels by controlling the ratios of carbon nanotubes to polymers in the dyestuffs. In this study, anionic polyurethanes, received as emulsions, were used as the typical polymers. The CNT-based dyestuffs have a life time (the mean diameter of CNTs monitored using the dynamic light scattering size distribution analyzer was used as the essential indicator) longer than 18 months.

Commercially available polyester multifilament yarns (20 dtex/24 filament) were dyed directly through a dye-printing approach (Fig. 2). Briefly, the polyester multifilament yarns were passed through a dye-bath containing the CNT-based dyestuffs. Temperature of the dye-bath was maintained at 40 ˚C. A micro-wave vibration system was used to vibrate the polyester multifilament yarns, so that each filament of the multifilament yarns was dyed thoroughly by the CNT-based dyestuffs. The CNT-dyed multifilament yarns were further cured at 170 ˚C , which was about 100 ˚C higher than the glass transition temperature (Tg, 69 ˚C) of the polyester multifilament yarns, for about 30 seconds, by passing the yarns through a cure oven. The resulting CNT-dyed multifilament yarns were black yet bright (Fig. 3). SEM images of the CNT-dyed multifilament yarns (Fig. 4) revealed a CNT-skin, with the CNTs arranged into continuously interconnected networks over the surfaces of the yarns. Each filament was coated by a continuous CNT-skin, with a coating thickness of approximately 400 nm. The outer skin, established by the continuously interconnected CNT-networks, functions as an electrically conductive layer (ECL) and the value of its electrical resistivity ranged from 10^3 to 10^9 ohm/cm, as verified by the contents of CNTs in the ECL.

Electrical resistivity measurements, obtained using a two-electrode resistance measuring meter (Table 1), demonstrated a highly uniform resistivity along the yarn direction. Furthermore, the CNT-dyed multifilament yarns have shown excellent stable electric resistivity, even under elongation. The yarns broke at an elongation ratio of approximately 30%.

The 10^3 ohms/cm level CNT-dyed multifilament yarns were woven into fabric (20 m × 0.6 m) by using the CNT-dyed yarns as the wefts (horizontal yarns) and the regular polyester textured yarn for the warps (vertical yarns). This orthogonally blended fabric was then cut into pieces of smaller size (20 cm × 30 cm) to evaluate their thermoelectric behaviors by gripping both ends of the CNT-dyed yarns of the fabric samples between two copper plates (electrodes). Typical plots of the time-temperature dependence, over the applied voltage range of 5 - 40 V (Fig. 5) illustrated that the orthogonally blended fabric functioned as an electrical heater when the applied voltages exceeded 20 volts.

The CNT-dyed multifilament yarns showed excellent electrical conductivity even after being water-washed. For example, for the 10^5 ohm/cm level CNT-dyed multifilament yarns, the electrical resistivity was 2.52×10^5 ohm/cm prior to washing and 8.23×10^5 ohm/cm (the average value of twenty measurements) after 20 min of washing in tap-water at 75 ˚C. This high tolerance for washing indicated that the CNT-dyed multifilament yarns are useful for anti-static uniforms.

CNT-dyed multifilament yarns with an electrical resistivity level of 10^9 ohm/cm have been used for establishing brushes for the photocopying machines; excellent static-control performance was obtained.

In conclusion, polyester multifilament yarns with each filament being suffused with a continuous CNT-skin can be produced in industrial quantities by using CNTs at the molecular level of dispersions as dyestuffs. This thin CNT-skin functions as an electrically conductive layer with excellent adhesion, toughness, and durability. The direct use of CNTs in dyeing opens new applications of nanotechnologies in yarn/textile productions.

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Table 1 Data on measuring of electric resistivity (ohm/cm) of twenty randomly chosen samples (10 cm of each sample) of the 10^3 ohm/cm level CNT-dyed multifilament yarns.

Samples	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
Resistivity (× 10^3)	1.76	1.65	1.91	2.01	1.65	1.78	2.03	1.72	1.92	1.76
Samples	#11	#12	#13	#14	#15	#16	#17	#18	#19	#20
Resistivity × (10^3)	2.01	1.78	2.00	2.03	2.01	1.90	1.72	1.70	1.76	1.70

Figures and Captions

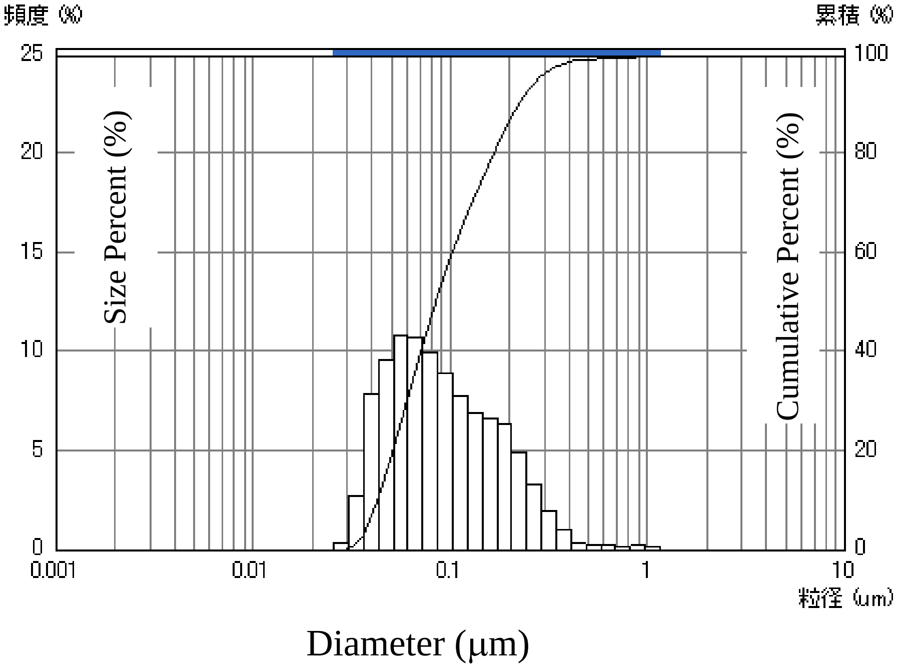

Fig. 1. Dynamic light scattering size distribution of CNTs in the CNT-based dyestuffs.

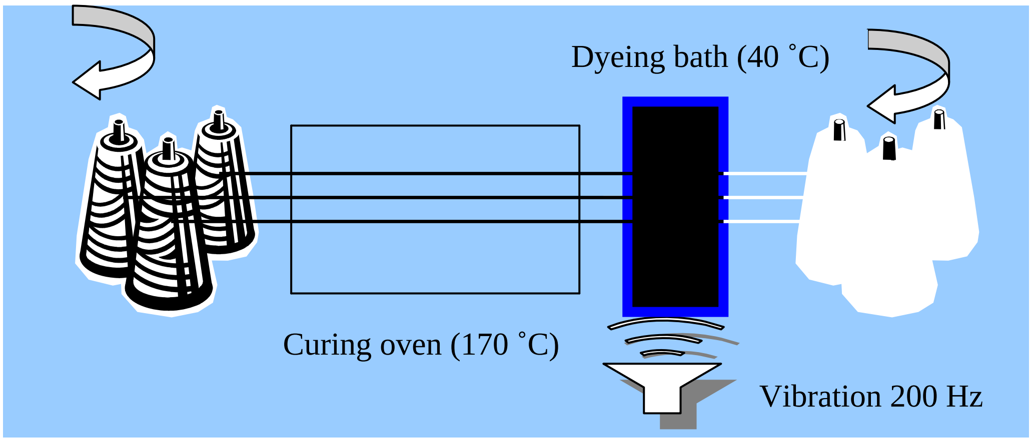

Fig.2. Schematic illustration of the dye-printing system for mass production of the CNT-dyed multifilament polyester yarns.

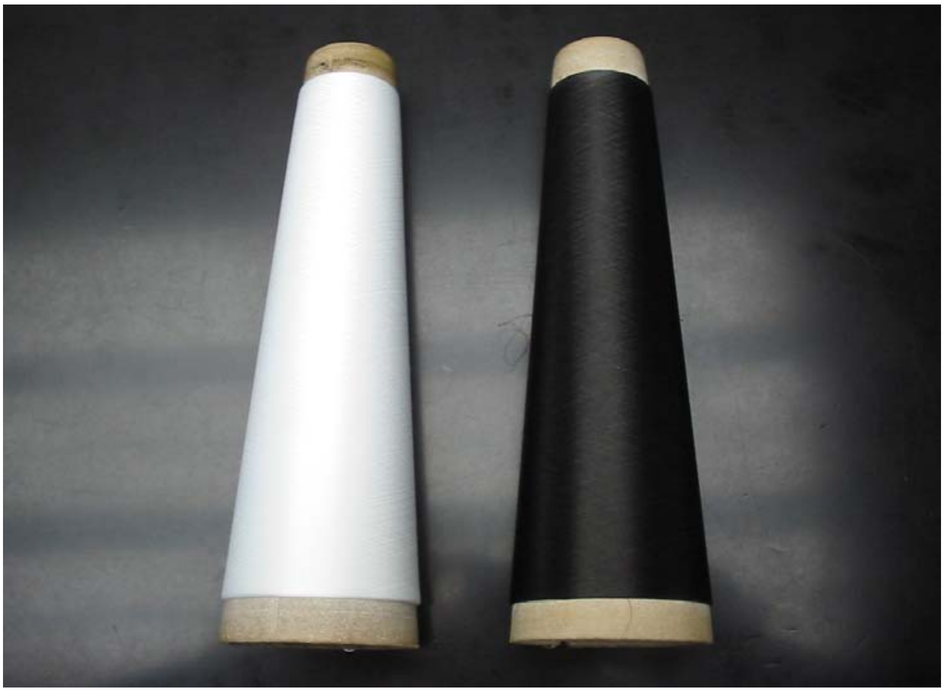

Fig. 3. Photos of the polyester multifilament yarns before (left-photo) and after (right-photo) being dye-printed with the CNT-based dyestuffs. The yarns were about 10,000 meters long.

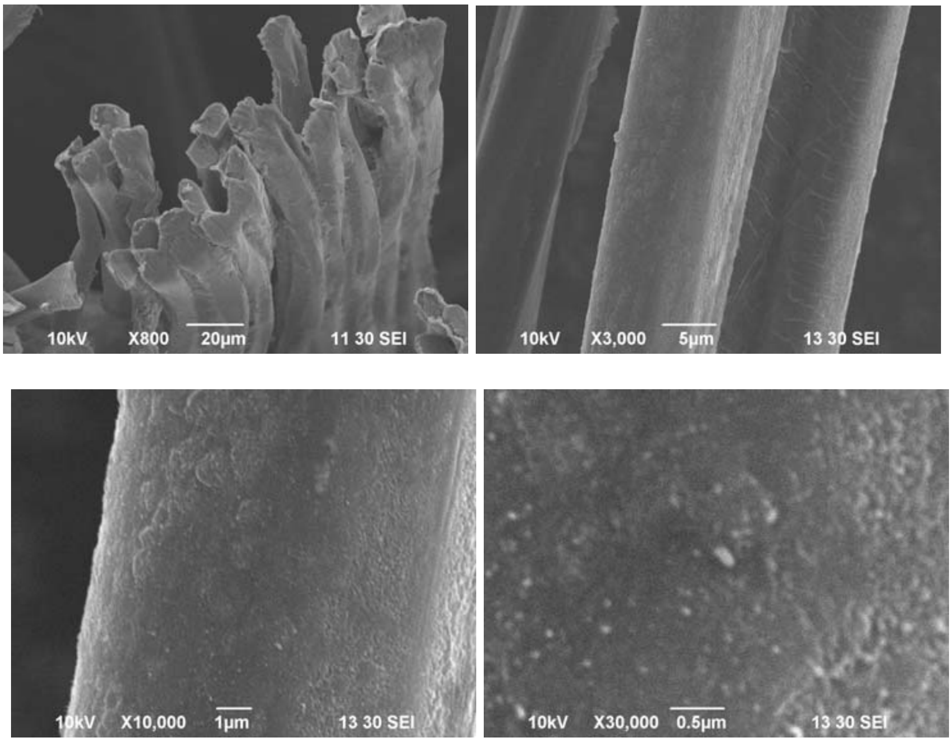

Fig. 4. SEM images of the CNT-dyed multifilament yarns. CNTs have established an electrically conductive layer with the individual carbon nanotubes arranged as a continuously interconnected network over each filament of the yarns.

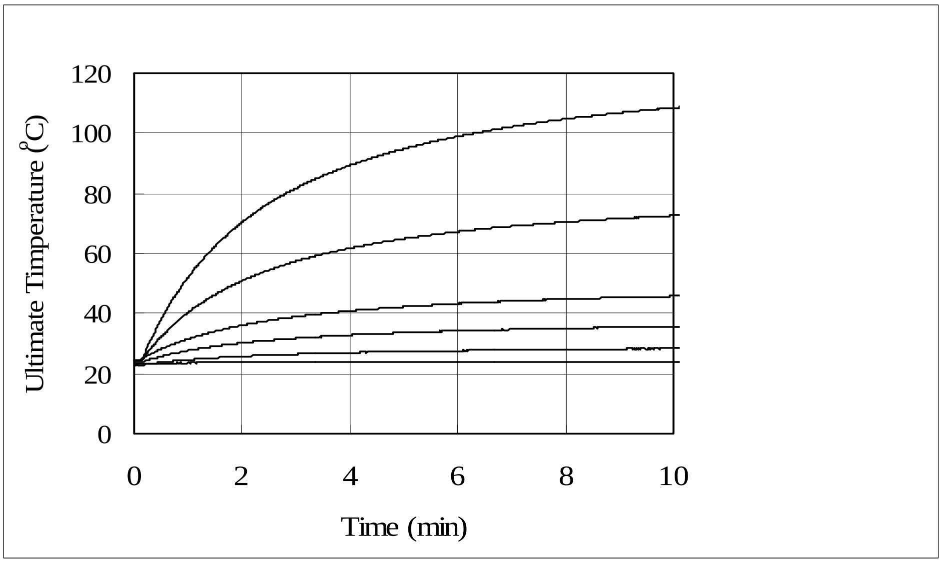

Fig. 5. Temperature-time dependence observed for the fabric samples obtained using CNT-dyed 10^3 ohms/cm level multifilament yarns as the wefts and regular polyester textured yarn for the warps. The applied voltages were 5, 10, 15, 20, 30, and 40 volts, respectively (from the bottom curve to the top curve).