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Carbon Nanotube Composite Films with Switchable Transparency

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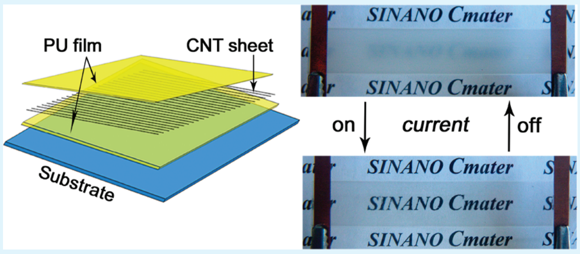
ABSTRACT: A composite film with switchable transparency is fabricated by sandwiching a carbon nanotube (CNT) sheet within polyurethane (PU) films. The introduction of CNTs not only makes the composite film electrically conductive but also induces a rapid crystal melting of soft segments in the PU. As a result, the film can be switched from opaque to transparent in just several seconds after turning on voltage, and reversed back to opaque after turning off voltage. The film also possesses several other attractive properties, including excellent flexibility, low energy consumption, switching speed insensitivity to ambient temperature, and easy coloration, which make the film promising for a wide variety of practical applications.



KEYWORDS: carbon nanotube, polyurethane, composite film, switchable, opaque-to-transparent transition

INTRODUCTION

Optically switchable windows (OSWs) have attracted great interest in areas of privacy and solar control, such as electrical shutters, smart auto windows, projection screen, and band-pass filters.[1,2] In fabrication of conventional OSWs, the coating of chromic materials on transparent indium tin oxide (ITO) allows the control of incident light transmission when an electric, thermal, or chemical stimulus is applied.[3−5] However, because of the shortage of indium in the earth's crust and the increasing demands for flexible transparent devices, it has been imperative to develop new technologies and manufacture low-cost, non-ITO-based multifunctional OSWs.

Recently, transparent carbon nanotube (CNT) sheets have attracted attention for a wide variety of applications, including electronics, conductors, loudspeakers, heaters, and incandescent displays.[6−13] Here, we report a CNT/polyurethane (PU) composite film with switchable transparency. The film becomes transparent under a voltage, and reverses back to opaque after the voltage turn-off. The existence of CNTs, at a very low concentration of 0.009−0.015 wt %,[14] effectively enhances the crystal melting of PU, and enables an opaque-to-transparent transition within a few seconds. The transparency switch is rapid and insensitive to environments, i.e., the transition can happen at a low temperature. Because of the simple synthesis method and today's ability to grow spinnable CNT arrays, the film technology developed here is easily scaled up for commercial production.

EXPERIMENTAL SECTION

The sandwich structure of the CNT/PU composite film is shown in Figure 1a. In this multilayer structure, the first layer of PU film was prepared on a glass substrate by evaporating the solvent of the PU solution. The thickness was controlled to be smaller than 0.01 cm, by adjusting the quantity of the solution. After the evaporation, a CNT sheet drawn out from a spinnable CNT array was laid directly on the PU film. The CNT sheet was $\sim$50 nm thick[7] and negligible to the total thickness of the composite film. Copper electrodes (not shown here) at the two ends of the CNT sheet were then prepared for the electrical conductivity measurement, similar to a method reported recently.[13] In such a way, electrodes had the maximum contact area with the sheet, and the total electrical resistance of the composite film was proportional to the film length. Finally, another PU film was covered on the sheet, also by evaporating the solvent. The thickness of the composite film was usually 0.015−0.02 cm, and it was hardly detectable the thickness dependence of the transparency.

The CNT sheet was transparent (Figure 1b) and was drawn out from vertically aligned CNT arrays synthesized by a catalytic chemical vapor deposition method.[15] Parameters concerning the growth, including the carbon source, catalyst, and growth temperature and time, were reported by our previous studies.[16−18] According to the tube structure, the arrays were divided into two groups, the few-walled (FWCNT, diameter ≤6 nm and 2−3-walled) and multiwalled (MWCNT, diameter 8−10 nm and $\sim$6-walled) arrays. The raw PU provided by Changzhou Sanhekou Polyurethane Factory was synthesized using 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) as the hard segments and aliphatic polyester polyol (PEP) as the soft segments. The PEP was the Product PBNA from the factory, and had a molecular weight of 2000−3000. The mole ratio of MDI/BDO/PEP was 4/3/1, and the concentration of hard segment in pure PU was 30−39 wt %. It should be noted that because of the large molecular weight, the

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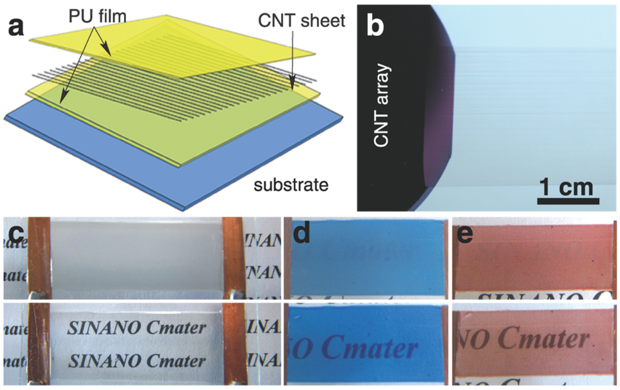

Figure 1. (a) Layered structure of a CNT/PU composite film. (b) A transparent and uniform MWCNT sheet is drawn from an array. (c) An opaque composite film is connected to two copper electrodes (top), and becomes transparent when an electric current is passing through the film (bottom). (d, e) The current-induced transparency (from top to bottom) is also observed in two dyed films.

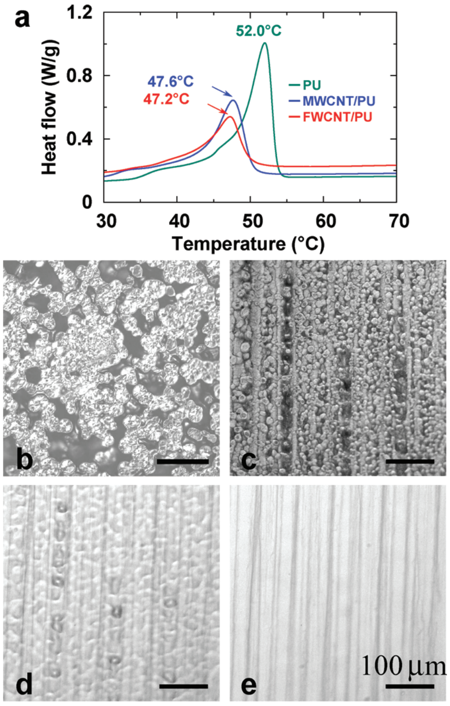

Figure 2. (a) DSC scanning of PU, MWCNT/PU, and FWCNT/PU films. (b) POM image showing the large-size spherulites (15−40 μm) in the pure PU. (c−e) POM images of an MWCNT/PU film at 0, 5, and 15 s, after connected to a voltage of 30 V. After the voltage turn-off, the composite film can recover back to (c). Scale bars are all 100 μm.

PEP molecules crystallized in forms of spherulites. Therefore our PU was opaque at room temperature. A similar phenomenon was also reported where the PU based on polycaprolactone diol (PCP) became opaque only when the molecular weight of PCP was larger than ~3000.[19] The PU was dissolved in *N,N*-dimethylformamide or 1-methyl-2-pyrrolidone, with a concentration of 10−20 wt %.

Differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were used to characterize the thermal dynamics of the PU. The DSC measurement was performed over a temperature range of 25−200 °C using a Seiko DSC-6220 thermal analysis system, with a heating rate of 2 °C/min. The transmittance of the composite film was determined with an Analytik Jena's SPECORD S600 spectrometer. To characterize the ohmic heating, we measured the temperature by an Optris CT LT infrared thermometer. Tensile tests were also performed using an Instron 3365 test machine with a strain rate of 0.5 mm/min and a gauge length of 10 mm.

RESULTS AND DISCUSSION

The composite film, initially opaque (Figure 1c, top), became transparent in just a few seconds when a certain voltage was applied (Figure 1c, bottom). It turned back slowly to the opaque state when the voltage was turned off. This film was 2.8 cm long (along the CNT direction), 1.2 cm wide, and ~0.015 cm thick. The reversible change between opaque and transparent can be also observed in two dyed CNT/PU films (length ~1.5 cm), see images d and e in Figure 1. The film length is always provided because the working voltage linearly increases with the length.

Without the introduction of CNTs, the opaque-to-transparent transition is simply a thermal effect of the soft segments which undergo a crystal melting at 52 °C, as indicated by the endothermic DSC peak for a PU film (Figure 2a). Before the melting, the soft segments crystallized in randomly distributed large-size spherulites, see the POM image in Figure 2b. After the transition (not shown here), the spherulitic soft segments turn to amorphous due to the disassembly and entanglement of the PEP molecules, similar to the melting-induced shape memory of PU.[20,21] At room temperature, the spherulites and their boundaries scatter and prevent the incident light from traveling through. When melted into amorphous structures, the soft segments have the ability to refract, reflect, and transmit light, without scattering it.

After CNTs are introduced, the PU film becomes electrically conductive, with a relatively high resistance. As a result, the film can turn to transparent because of an ohmic heating (Figure 1c−e) under an electric current. Note that the transition is not simply a thermal effect as observed in the PU film, because the crystallization kinetics and thermal behavior of the soft segments have changed significantly. For example, the melting temperature has decreased from 52 °C to ~47 °C due to the existence of MWCNTs or FWCNTs (Figure 2a). This decrease probably arises from the changes in size and alignment of the spherulites. Figure 2c−e show POM images of a 1.4-cm-long MWCNT/PU film at 0, 5, and 15 s, respectively, after the application of a 30 V voltage. The spherulites are found to crystallize along CNT bundles, with an average size of ~15 μm (Figure 1c), which are different from those randomly distributed ones with the size ranging from 15 to 40 μm in the pure PU (Figure 2b). The aligned small spherulites, as well as their size uniformity, are induced by the spacing between CNT bundles which could be up to 20−30 μm (Figure 2c), and more importantly, by the strong interaction between CNT and aromatic MDI molecules. These molecules serve as connecting points for the soft copolymers, and accumulate near the CNT surfaces due to the π-conjugation. Therefore, the soft segments form spherulites near CNT bundles with an appropriate size for easy transition to amorphous structure under heating.

CNTs also make the transparency switching more rapid than that of the pure PU, and interestingly, less sensitive to the environmental temperature. It usually takes 15−20 s for a PU film to be transparent on a hot stage with a temperature of 60 °C.

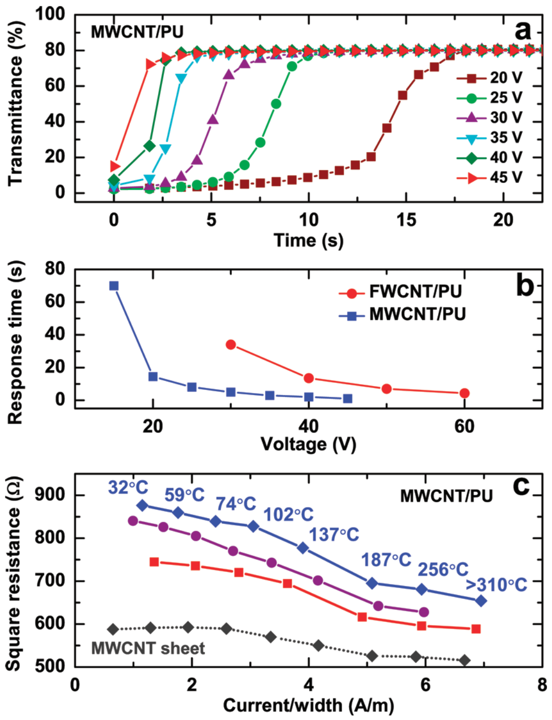

Figure 3. (a) Time evolution of 550 nm transmittance for an MWCNT/PU film connected to various voltages. Due to the slow response, the result at 15 V is not shown. (b) Response time obtained from (a) for different composite films. The films were both 1.4 cm in length. (c) Square resistances of three MWCNT/PU films and an MWCNT sheet as functions of electric current per unit film width. The resistance decreases because of the enhanced electron hopping between CNTs, a result of the temperature increase. In one plot, the film temperature is also provided.

However, the 1.4-cm-long MWCNT/PU film can be transparent in less than 5 s when connected to a voltage higher than 30 V, see Figure 3a. The film exhibited the same fast switching of transparency at a low temperature of 0−4 °C inside a refrigerator. This temperature insensitivity ensures the application of the film at low temperatures. The response time as a function of voltage is plotted in Figure 3b, which is defined as the time to reach the half of the full transmittance (about 80% and 90% for the MWCNT/PU and FWCNT/PU films). With increasing voltage, the response time decreases. The slower response of the FWCNT/PU film is due to its larger electric resistance. The square resistance[22] of such film was ∼1950 Ω/□, measured at 0 V, more than doubled than that of the MWCNT/PU film (∼900 Ω/□).

Because of the ohmic heating, the temperature increases when an electric current passes through the film. The temperature could become surprisingly high for a pure CNT sheet in vacuum, up to 1−1.5 × 10^3 K under a 100-mA current.[10] As a result, the electrical conductivity changes as the hopping of electron between CNTs is enhanced.[23,24] In Figure 3c square resistances in air of three MWCNT/PU films and a pure MWCNT sheet were plotted against the current normalized by film width. It clearly shows a decrease in resistance with increasing current. When the current was smaller than 1 A/m, the temperature of the composite films was 30−40 °C, below the melting temperature. Therefore the film remained opaque. The applied voltage, for the 1.4-cm long film, was 10 V. When it was increased to 20 V, the film temperature became 74 °C, and it took about 15 s to complete the opaque-to-transparent transition (Figure 3a). Further increase in voltage resulted in more rapid transitions. However, when the voltage was higher than 35 V, corresponding to a current of ∼4.5 A/m, the film temperature was very close to 200 or higher and could do harm to real applications. Therefore the safe working current should be no larger than 4 A/m. A smart way to use such temperature-current relation is to activate the transparency at a high voltage (30−35 V) and maintain the transparency at a low voltage (<15 V).

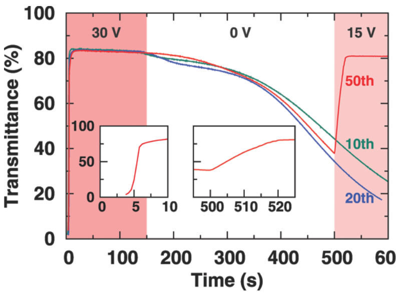

Figure 4. Transmittance of an MWCNT/PU film as a function of time, for the 10th, 20th, and 50th switches of transparency. The voltage was 30 V in the beginning 150 s. Especially for the 50th switch, the voltage was set to 15 V at 500 s.

The composite film could change the transmittance repeatedly, at least more than 50 if the current was smaller than the safe one, see Figure 4 where repeated time evolutions of an MWCNT/PU film were shown. However, the reverse change (from transparent to opaque) was much slower, and the transmittance was still higher than 50% about 5 min after the voltage turn-off. Specially for the 50-th change, we turned the voltage to 15 V at 500 s. As the soft segments were not fully crystallized, it took only 20 s to return transparent. It means that the maintenance voltage can be applied for just seconds per several minutes. We have tried this approach and found that the power consumption was only 0.01 W/cm^2.[25]

The low energy consumption of the transparent composite film is due to the small thermal conductivity of PU (∼0.2 W/mK for the nonporous PU),[26] which is several orders of magnitude smaller than those of copper (401 W/(m K)) and CNTs (∼3000 W/(m K)). It slows the heat dissipation into the surrounding ambient environment, and therefore improves the transition rate and reduces the energy consumption to maintain transparency.

Besides the optical, electrical, and thermal properties, the composite film also has a good mechanical behavior under external strains. Because of the small CNT mass fraction, the pure PU and composite films all showed a tensile strength of 6−10 MPa at yield and of 15−20 MPa at break (larger than 400%), and a high initial modulus of 270−325 MPa (derived from the linear stress−strain relationship up to 2−3%). The composite films were also flexible, i.e., they could be peeled off the substrate readily and transferred onto objects with various geometric shapes.

As a new developed functional material, there is still a large room to improve the performance. For example, the voltage threshold to activate the transparency switching depends on the electrical resistance of the film (Figure 3b). To make the transparency switch at lower voltages, we should use highly conductive CNT sheets. This could be realized by coating metal nanoparticles on the CNT sheets. We found that this coating could decrease the square resistances of both the FWCNT and MWCNT sheets by 1 order of magnitude without losing the transparency (to be reported elsewhere). Therefore, the switch efficiency can be dramatically improved.

CONCLUSIONS

In summary, we have demonstrated a novel and facile approach to fabricate CNT-based composite film with switchable transparency. The incorporation of CNT sheet into PU films, even at a very low mass fraction of <0.2 wt %, results in small and aligned spherulites of soft segments along CNT bundles, and a lower melting temperature than in a pure PU film. The composite film can be electrically conductive, flexible, and switchable from opaque to transparent under various environments if an electric current passes through it. Because of the easy synthesis and sufficiently low power consumption to maintain the transparency, such a method can be used in large-size OSWs at a very low energy cost.

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