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Surface modification of plastic substrates via corona-pretreatment and its effects on the properties of carbon nanotubes for use of flexible transparent electrodes

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ABSTRACT

In this study, the surface of polyethylene terephthalate (PET) substrates was modified via corona treatment before the deposition of carbon nanotubes (CNTs), and the effects of such surface modification on the properties of the CNTs for flexible transparent electrodes were investigated. The changes in the surface roughness, contact angle, and surface energy of the PET substrates due to the corona treatment were characterized in terms of the applied corona energies, PET feeding directions, and treatment times. The higher corona energies, the more frequent treatment times, and the bi-directional treatment produced the larger surface roughness of the PET substrates. The results of the contact angles and the surface energies indicated that the surfaces of the PET substrates became hydrophilic from hydrophobic after the corona treatment. The analysis using X-ray photoelectron spectroscopy confirmed that oxygen polar groups appeared when the PET substrates were corona-treated. In addition, the increase in the CNTs' sheet resistance values due to their repeated outer and inner bending (up to 16,000 times) was found to have been significantly alleviated when the CNTs were deposited on the corona-treated PET substrates. This confirmed that the adhesion of the CNTs was improved after the corona pretreatment of the PET substrates.

1. Introduction

Carbon nanotubes (CNTs) have been considered among the transparent conductive (TC) materials that can potentially replace the conventional indium-tin-oxide (ITO) films [1,2]. Also, CNTs are fast becoming ideal candidates for use in flexible electronics due to their unique properties such as their high intrinsic carrier mobility and conductivity, mechanical flexibility, and potential for production at a low cost [3–5]. For the flexible applications, CNTs are required to be deposited on plastic substrates such as polyethylene terephthalate (PET), polyethylene (PE), and polypropylene (PP) substrates [6–8]. To deposit the CNTs on the plastic substrates, various methods, including spray-coating [9], dip-coating [10], bar-coating [11], and inkjet printing [12], have been used. However, these methods have common problems, such as weak adhesion between the plastic substrates and the CNTs [13]. This is mainly because the plastic substrates have no polar groups on their surfaces.

Surface modification processes, which generally oxidize the top polymer layer of the plastic substrates, have been performed using various methods, such as helium plasma treatment, the UV method, and chemical modification with sodium hydroxide [14–16]. However, most of these methods have a problem, such as a low working pressure, long treatment time, and high process temperature. As a commercially favorable method of surface modification of plastic substrates, corona pretreatment has been suggested because it can be carried out at atmospheric pressure and room temperature [17,18]. The ability to modify the surface properties of the material without changing its bulk characteristics is another advantage of corona pretreatment. However, systematic studies on the effects of corona treatment on the properties of CNTs as flexible electrodes have scarcely been reported in literature.

In this study, surface modification of PET substrates was carried out via corona discharge before the deposition of the CNTs, and its effects on the properties of the CNTs as flexible transparent electrodes for touch screen panels were investigated extensively. The corona treatment of the PET substrates was performed by varying the corona energies, PET feeding directions, and numbers of corona treatment. The CNTs were spray-coated on the untreated and corona-treated PET substrates. The changes in the surface morphologies, contact angles, surface energies, and surface chemistries of the PET substrates due to the corona treatment were systematically analyzed. Also, the changes in the sheet resistance values of the CNTs due to bending (for up to 16,000 times) were measured according to the PET substrates that were corona-treated and untreated. The results of the experiment in this study demonstrated

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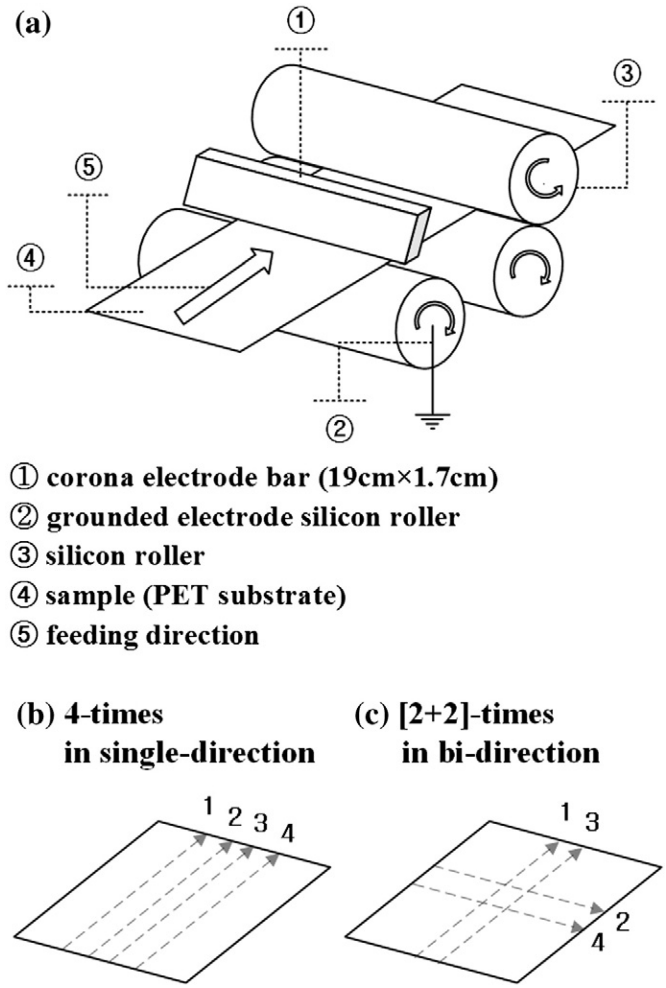

Fig. 1. The schematic diagram (a) shows the corona-discharge system used in this study. The diagrams (b) and (c) illustrate the corona-treatment methods, including the feeding directions of PET substrates and the number of treatments, such as (b) 4-times of treatment in single-direction and (c) [2 + 2]-times of treatment in bi-direction respectively.

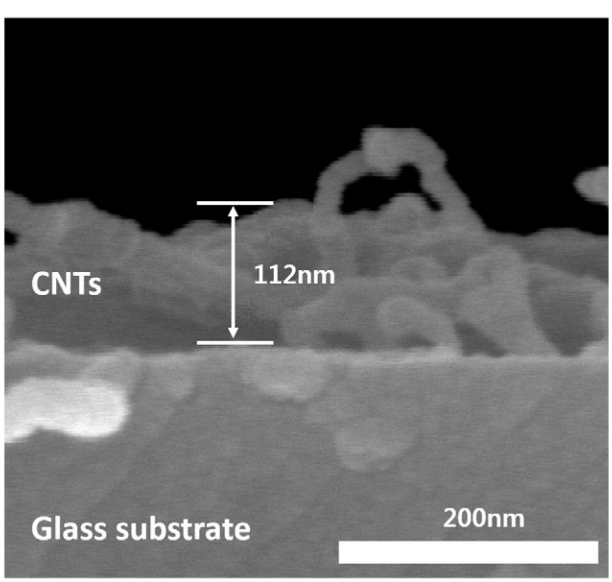

Fig. 2. Cross-sectional FE-SEM images of the CNTs deposited on the glass substrate.

that the adhesion of the CNTs can be enhanced remarkably by the surface modification via the corona-discharge pretreatment of the PET substrates.

2. Experiment

Before the deposition of single-walled CNTs (Hanwha Chemical Corp., ASP-100F), the PET substrates (SKC, Skyrol, 100 μm thickness) were treated using corona discharge for surface modification. Fig. 1(a) shows the schematic of the corona discharge system. Fig. 1(b) and (c) illustrates how the corona treatment was performed, including the feeding directions of the PET substrates and the numbers of treatments, such as once, 2-times, and 4-times for the single-directional treatment, and [1 + 1]-times and [2 + 2]-times for the bi-directional treatment. The corona discharge was generated by applying 8 kV voltage to a corona electrode (1.7 cm × 19 cm), and the PET substrate passed between two electrodes (i.e., the corona electrode and the grounded electrode) at a specified speed for surface treatment. The corona energy was controlled by varying the substrate feeding speed. The corona energy densities were controlled to be increased from 149 kJ/m^2 to 5263 kJ/m^2 by decreasing the feeding speed from 17 m/min to 0.5 m/min. Also, the substrate feeding directions and the number of treatments used in the corona treatment were the single direction (once, 2-times, and 4-times treatments), and the mutually vertical bi-direction, with [1 + 1]-times and [2 + 2]-times treatments. Also, after the corona treatment, ultrasonication was performed in an acetone solution for 5 min and in ethanol and deionized-water solutions for 10 min each.

The suspension that was used to deposit the CNTs was manufactured through purification and dispersion as follows. First, the CNT powder

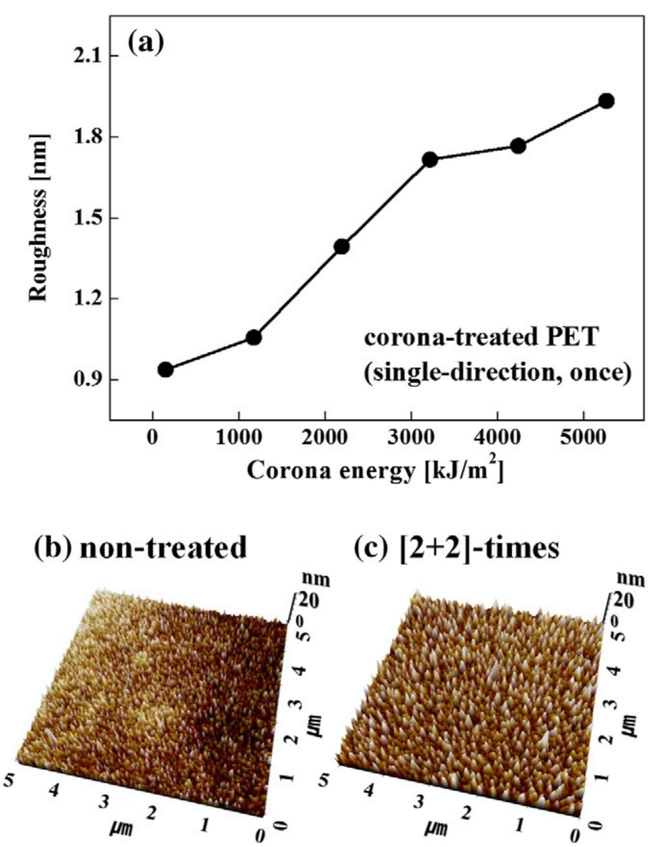

Fig. 3. Shows the change in the surface roughness (σ_{rms}) estimated from the AFM measurement in terms of the corona energy density. (b) and (c) display the AFM surface images obtained from the PET substrates which were non-treated and corona-treated ([2 + 2]-times at 5263 kJ/m^2 in bi-direction) respectively.