ผลของการลดแรงตึงผิวและความหนาของฟิล์มท่อนาโนคาร์บอนต่อสมบัติการนำไฟฟ้าสำหรับจอสัมผัส
Effect of surfactants and thickness of carbon nanotube film on conductive property for touch screen

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บทคัดย่อ
เทคโนโลยีฟิล์มโปร่งใส นำไฟฟ้าได้รับการพัฒนาอย่างกว้างขวางสำหรับอุตสาหกรรมอิเล็กทรอนิกส์ เช่น จอแสดงผล จอสัมผัสและอื่นๆ งานวิจัยนี้ศึกษาผลของสารลดแรงตึงผิวและความหนาของฟิล์มท่อนาโนคาร์บอนแบบชั้นเดี่ยวหรือชั้นเดี่ยวกระจายตัวในอะคริลิกเรซิ่น และสารลดแรงตึงผิวชนิดไอโดรคาร์บอนกับซิลิโคนที่ความเข้มข้นระดับต่างกัน ช่วยการกระจายตัวของฟิล์มในคาร์บอน การกระจายตัวของฟิล์มในคาร์บอนนี้เป็นหนึ่งในปัจจัยสำคัญที่มีอิทธิพลอย่างมาก ต่อสมบัติการนำไฟฟ้าและความโปร่งใสของฟิล์ม โดยใช้เทคนิคการเคลือบด้วยแท่งขดทางเคลือบสารท่อนาโนคาร์บอนแบบชั้นเดียวและหลายชั้นบนพลาสติก ให้ความหนาต่างกัน งานวิจัยพบว่า Dow corning 193C ซึ่งเป็นสารลดแรงตึงผิวชนิดซิลิโคนช่วยการกระจายตัวของฟิล์มในคาร์บอน ซึ่งส่งผลให้การนำไฟฟ้าที่ดีกว่า Triton X-100 ที่เป็นสารลดแรงตึงผิวชนิดไฮโดรคาร์บอน โดยค่าความด้านทานของฟิล์มต่ำสุดที่ 8.91x10^2 โอห์มต่อตารางนิ้ว ค่าความโปร่งใสของฟิล์มเป็นร้อยละ 87 และ 2.63x10^3 โอห์มต่อตารางนิ้ว ค่าความด้านทานของฟิล์มมีค่า 2.0 ของสารลดแรงตึงผิวชนิดซิลิโคน และไฮโดรคาร์บอน ผลลัพธ์ที่ความหนา 250 ไมโครเมตร

คำสำคัญ: ฟิล์มในคาร์บอน สารลดแรงตึงผิว ฟิล์มโปร่งใส เทคนิคการเคลือบแบบเส้นลวด

Abstract
Conductive transparent film technology has been developed extensively for the electronics industry such as display, touch panel and so on. We studied the effects of surfactants and thickness of single-walled carbon nanotube (SWCNT) film on conductivity and transparency. The wire-bar coating technique was used to produce a conductive PET film base. Triton X-100 is Hydrocarbon and Dow corning 193C fluid is silicone non-ionic surfactant types were chosen by varying concentration to disperse the single-walled carbon nanotubes (SWCNT) in acrylic resin. Multi coating technique was proposed to obtain different thickness. Results showed Silicone surfactant gave better results than Hydrocarbon surfactant, the optimum sheet resistance was at 8.91x10^2 Ω/sq with 87% transmittance (including PET film) and 2.63x10^3 Ω/sq with 86% transmittance by using 2.0% of silicone and hydrocarbon surfactant respectively with the film thickness of 250 microns.

Keyword: Conductive transparent film, Carbon nanotube, Surfactant, Wire-bar coating technique
1. Introduction

Conductive transparent film (CTF) is an important component of modern electronic devices such as display, touch screen, solar cell, sensor and so on. Indium tin oxide (ITO) is the most commonly known, but it suffers from the problem of limited production capacity. It is because it is a rare mineral and high cost. Carbon nanotube (CNT) can be used as a conductive transparent film. It is due to its two main properties: conductivity and optical transparency. It also has high flexibility. Structure of carbon nanotubes are a cylindrical tube comprised of six-molecule carbon ring, as in graphite, with a diameter in nanometer scale. Techniques have been developed to produce nanotubes in sizable quantities, including arc discharge, laser ablation, chemical vapor deposition (CVD) and high-pressure carbon monoxide disproportionation (HiPCO) and two mains type of carbon nanotubes are single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) [1].

Single-Walled Carbon Nanotubes are defined as a one dimensional, cylindrically shaped allotropes of carbon that have a high surface area, small size, with a diameter between 0.7-2.0 nm. The structure is easy to analyze, can be easily twisted and flexible more than multi-walled carbon nanotubes. SWCNT can exhibit either metallic properties or semiconducting properties, depending upon the characterized by three different structures. There are typically three types of single-walled carbon nanotubes that can form, these are: the armchair, zig-zag, and chiral.

SWCNT dispersions were prepared in aqueous solution, carbon nanotubes are not well distributed. Therefore the surfactant is used to help dispersing. There are four types of surfactants, according to the hydrophilic head of the molecules; there are cationic surfactant, anionic surfactant, non-ionic surfactant and amphoteric surfactant. The hydrophobic tails of most surfactants are fairly similar, consisting of a hydrocarbon chain, which can be branched, linear, or aromatic and silicone surfactants have siloxane chains [2-4].

PET film is the most popular plastic as it is clear, lightweight, strong, impact-resistant and heat resistant up to 250°C. It makes a good gas and fair moisture barrier. In addition to choosing plastic types, the transparency of plastics is also important because difference for application. For example, the display has 80% transparency and the touch screen has 85-90% transparency.

Regarding the study about the adhesion effect of carbon nanotubes on polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) using dip coating [5], it reported that the thickness of the film layer affected the sheet resistance and transparency. In addition, the electrical conductivity of indium tin oxide was better than carbon nanotubes, but the transparency of SWCNT was better than ITO and MWCNT [6].
Thus, the preparation of carbon nanotube film with surfactants using proper coating method can be considered as important factors [7]. For example, the silicone surfactant was used in dispersion of carbon nanotubes in the water base system [8]. Our objectives were to study the effects of surfactants and thickness of single-walled carbon nanotube (SWCNT) film on conductivity and transparency using the single and multi-coating technique by wire-bar coater was used to produce a conductive film PET base and preparation SWCNT dispersion with hydrocarbon and silicone non-ionic surfactant types were varied concentration and thickness coating.

2. Experimental

2.1 Chemicals and materials

A hydrocarbon surfactant Triton X-100 and SWCNTs were supplied by Sigma-Aldrich Co., Ltd., The SWCNT was prepared by a catalytic chemical vapor deposition (CVD) method with 1 µm length. The silicone surfactant, ethoxy modified trisiloxane was purchased from Dow corning Co., Ltd. Acrylic copolymer dispersion (Neocryl A-1127) was purchased from DSM. Poly(ethylene terephthalate) (PET) sheets (91% transparency, 125 µm thickness) were supplied by Virtiflex Co., Ltd.

2.2 Preparation of PET films

The surface of PET film was treated by corona treatment. Using a dyne test pen test, the surface energy was increased up to >50 dyne. The PET films was soaked in methanol in 30 min to remove the dispersant reagent and dried in an oven at 80ºC for 5 min.

2.3 Preparation of SWCNT solution

We prepared 10.0 mg of SWCNT to disperse in 10 g acrylic solution with difference type and concentration of surfactant varied 0.1-2.0% w/w. Firstly, acrylic resin/deionized water (1:1 w/w) and surfactants were mixed in a vial. A magnetic stirrer at 500 rpm for 30 min was employed to homogenize the acrylic solution. Secondly, the SWCNT was added to the solution using magnetic stirrer at 1500 rpm for 1 hour to disperse it and then to sonicate in a bath sonicator for 30 min.

2.4 Coating method

The SWCNT solution (4 ml) was drawn down by a wire-bar coater on surface treated PET film samples. The obtained coated SWCNT films were dried at 80ºC for 5 min.

The concentration of each surfactant was varied at 0.1, 0.2, 0.5, 1.0 and 2.0% w/w. To study the effect of concentration of surfactants, we used the wire-bar coated 50 µm size. While studying the effect of coating thickness, the wire-bar coaters at 24, 50, 80 and 100 µm size were chosen for single coating, and 100+50, 100+100 and 100+100+50 µm sizes for multiple coating.
2.5 Sheet characterization

Sheet resistance was measured using a 4-pin probe Keithley 2450 sourceMeter. Transmittance was measured using a spectrophotometer HunterLab. Scanning electron microscopic (SEM) observations were carried out using field-emission scanning electron microscope (accelerating voltage: 2.0 kV; JEOL JSM-7600F). SEM image was used to analyze the surface morphology of coated films.

3. Results

Figure 1 and 2 show the SEM images of SWCNT coated on PET films by varying the concentration of hydrocarbon and silicone surfactants respectively. The distribution of SWCNT was considered. It was found that higher surfactant concentration gave better SWCNT distribution, particularly at the surface of coated film. For example, we can see explicitly the distributed SWCNT at surfactant concentration 2% (e). This implied that there was less flocculation of SWCNT in the coated films. Compared with hydrocarbon surfactant, silicone surfactant resulted in better result of SWCNT distribution.

Fig 1. SEM images of SWCNTs coated onto PET film using hydrocarbon surfactant (a) 0.1% w/w (b) 0.2% w/w (c) 0.5% w/w (d) 1.0% w/w (e) 2.0% w/w
To consider sheet resistance R (Ω/sq) and transmittance T (%) of coated films, we found that there was relationship between the increase of surfactant concentration and sheet resistant value. From 0.1% to 2% of surfactant, the sheet resistant was decreased 63% and 57% for hydrocarbon and silicone surfactants respectively as the averaged data given in Table 1. Conversely, the transmittance of coated films showed similar manner, but the values slightly increased. Based on the optimum result we obtained in Table 1, we chose the proper surfactant concentration at 2.0% to continue the further experiment.

**Table 1.** Sheet resistance (R) and transmittance (T) of coated films

<table>
<thead>
<tr>
<th>Concentration of surfactant (% w/w)</th>
<th>Hydrocarbon surfactant</th>
<th>Silicone surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R (Ω/sq)</td>
<td>T (%)</td>
</tr>
<tr>
<td>0.1</td>
<td>$1.82 \times 10^5$</td>
<td>86.5</td>
</tr>
<tr>
<td>0.2</td>
<td>$1.25 \times 10^5$</td>
<td>87.3</td>
</tr>
<tr>
<td>0.5</td>
<td>$9.74 \times 10^4$</td>
<td>87.9</td>
</tr>
<tr>
<td>1.0</td>
<td>$8.12 \times 10^4$</td>
<td>88.0</td>
</tr>
<tr>
<td>2.0</td>
<td>$6.69 \times 10^4$</td>
<td>88.2</td>
</tr>
</tbody>
</table>
To consider the effect of coated film thickness, we used the wire-bar size values instead of thickness measurement after drying as we cannot measured the real thickness. Table 2 shows the averaged data of sheet resistance and Transmittance values of coated films with varying thickness by using different wire-bar sizes. It was found that there was a trend of sheet resistance decreasing when the thickness of coated films were increased. Interestingly, the transmittance values showed similar results. Multiple coating played an important role in increasing the thickness of coated films. We could achieve the optimum sheet resistance values $8.91 \times 10^2 \, \Omega/\text{sq}$ and $2.63 \times 10^3 \, \Omega/\text{sq}$ for silicone and hydrocarbon surfactants respectively by using multiple coating at 250 µm wet-film thickness. While % transmittance of coated films was slightly decreased not over 2% in our experiment. Note that the display devices available in the market today have a limit of % Transmittance values not lower 85%. Thus, we can say that it is possible to adjust the surfactant concentration and the thickness of coated SWCNT films to achieve the satisfied Sheet Resistance and % Transmittance. And the most important thing is the choice of surfactant.

Table 2. Sheet resistance (R) and transmittance (T) of coated films

<table>
<thead>
<tr>
<th>Wet film thickness (micron)</th>
<th>Hydrocarbon surfactant</th>
<th>Silicone surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R (Ω/sq)</td>
<td>T (%)</td>
</tr>
<tr>
<td>24</td>
<td>9.74 x 10^5</td>
<td>88.6</td>
</tr>
<tr>
<td>50</td>
<td>6.69 x 10^4</td>
<td>88.2</td>
</tr>
<tr>
<td>80</td>
<td>3.58 x 10^4</td>
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<tr>
<td>100</td>
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<td>87.1</td>
</tr>
<tr>
<td>150</td>
<td>9.89 x 10^3</td>
<td>86.8</td>
</tr>
<tr>
<td>200</td>
<td>5.86 x 10^3</td>
<td>86.3</td>
</tr>
<tr>
<td>250</td>
<td>2.63 x 10^3</td>
<td>86.1</td>
</tr>
</tbody>
</table>
4. Conclusions

We can improve the Sheet Resistance and % Transmittance of conductive SWCNT film by using single and multiple-coating technique of wire-bar coater. This depends on the concentration of surfactants and the thickness of SWCNT coated films. The increase of surfactant concentration affected the reduction of Sheet Resistance; while %Transmittance was increased. The increase of coated SWCNT film thickness affected the reduction of both Sheet resistance and Transmittance. Silicone surfactant gave better results than Hydrocarbon surfactant did.

References


