Electrical Characteristics of Carbon Nanotubes by Plasma and Microwave Surface Treatments

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The plasma and microwave surface treatments of carbon nanotubes that loaded on plastic substrates were carried out with expecting a change of carbon nanotube dispersion by increasing treatment time. The microwave treatment process was undergone by commercial microwave oven (800 W). The electrical property was measured by hall measurement and resistance was increased by increasing O₂ flow rate of plasma, suggesting an improvement of carbon nanotube dispersion and a possibility of controlling the resistances of carbon nanotubes by plasma surface treatment. The resistance was increased in both polyethylene terephthalate and polyimide substrates by increasing O₂ flow rate. Resistance changes only slightly with different O₂ flow treatment in measure rho for all polyimide samples. Sheet resistance is lowest in polyimide substrate not due to high carbon nanotube loading but due to tendency to remain in elongated structure. O₂ or N₂ plasma treatments on both polyethylene terephthalate and polyimide substrates lead to increase in sheet resistance.

Key Words: CNT dispersion, Microwave surface treatment, Atmospheric pressure plasma, Electrical property

Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Nanotubes have been constructed with length-to-diameter ratio of up to 132,000,000:1, significantly larger than for any other material. Since the discovery of CNTs which possess unique physical, chemical, and structural properties, researchers have concentrated on utilizing these remarkable characteristics for engineering applications such as polymeric composites, electronic devices, and field emission display and hydrogen storage. In regards to mechanical properties, a single-walled carbon nanotubes (SWCNTs) are known to be far stiffer than steel. For multi-walled carbon nanotubes (MWCNT), the modulus can approach 200-4,000 GPa. CNTs have a large aspect ratio with low densities. Due to these superior characteristics, CNTs have been commonly considered as potential filling material in polymeric nano-composites.

CNTs have high mechanical strength, high electrical conductivity, and excellent chemical stability. In numerous applications of CNTs, dispersion of CNTs in solvents is an important step to enhance the performance of CNTs. However, its poor solubility and dispersibility are problem to applications. CNTs are easily entangled from substantial van der Waals attraction between tubes to form agglomeration. Agglomeration is barely breakable by sonication or ball mixing, such as physical methods. Nanodispersion is necessary to fabricate nanotube transistor. Therefore, nanodispersion is recognized as an important first step toward various potential applications and an indispensable scientific goal for practical applications. In this study, therefore, we did atmospheric plasma and microwave surface treatments of carbon nanotubes loaded on plastic substrates to increase CNT dispersion.

Experimental

We prepared several substrates for CNTs loading such as polyimide (PI), polyethylene terephthalate (PET), and glass. Also, CNTs synthesized by arc discharge were purchased from Iijin nanotech CO. Ltd. The CNT powder was dissolved in 100 mL of H₂O solution with 2 wt % of sodium dodecylsulphate (SDS), which is a good surfactant for CNTs in water.

Two types of treatment experiment were investigated on the dispersion density and electrical property. Atmospheric pressure plasma (APP; Plasmart™, Miniplasma®) and microwave treatment were used for both surface treatment of substrate and control the dispersed CNTs density on each substrate. APP surface treatment was carried out with the following conditions; 600 W of RF power, 20 sccm of N₂ or O₂, and 20 s. Also microwave treatment was carried out using commercial microwave oven (800 W) with increasing the treatment time. Substrates were investigated by infrared (IR) spectroscopy and water contact angle measurement. The morphology of CNTs dispersion was investigated by scanning electron microscopy (SEM). Also, hall measurement was used for measuring the sheet resistance of CNTs dispersed samples.

Results and Discussion

Figure 1 shows the IR spectra and contact angle of each
substrate. PET and glass has relatively weaker CH peak than that of PI. OH peak is only showed with PET and glass substrates. PI has strong CH peak around 3000 cm$^{-1}$. Also, glass has strong OH peak due to water adsorption on SiO$_2$ surface while there is no OH peak in PI. Thus, wettability of glass is the highest in this experiment. The order of wettability is glass, PET, and PI in higher one. The average values of water contact angle of glass, PET, and PI are 70, 60, 50 degree, respectively. As the result, PI has the highest contact angle and glass has the lowest contact angle.

Figure 2 shows the SEM images of dispersed CNTs on various substrates. The morphology of CNTs on each substrate was influenced by surface wettability. Thus, amount of CNTs was increased by decreasing the contact angle. Also, amount of CNTs on plasma treated substrate is changed by reactive gas. Nitrogen plasma treated PET has more amount of CNTs than oxygen plasma treated PET because of difference of both wettability and plasma induced product yield. Nitrogen and oxygen plasma treatment could give different wettability on the surface due to different bond energy. Also, stable glow discharge of plasma induced lots amount of reactive species in the plasma. Thus, more stable plasma gives more wettability. Plasma stability was influenced by RF power, pressure, reactive gas amount, kind of reactive gas, etc. However, RF power, pressure, and gas flux is the same in this experiment. The key factor of stability is the kind of gas. In this experiment, nitrogen APP is more stable than oxygen APP. Thus, wettability of nitrogen APP treated sample is the highest in this condition.

Figure 3(a) shows the sheet resistances of the dispersed CNTs on each substrate with various plasma treatment conditions. The sheet resistance for untreated sample is the lowest in the all cases. Also, the sheet resistance was increased by surface APP treatment. Especially, it was increased with increasing the wettability. Thus, as shown in the Figure 3(a), untreated sample has the lowest resistance and nitrogen APP treated sample has the highest value since the product yields of oxygen ion species and oxygen radicals are much higher than those of nitrogen. In addition, there are relatively many C=O and C-O bonds in the CNTs after oxygen plasma treatment, resulting in small decrease of sheet resistance compared with that of nitrogen plasma treated CNTs that contained only single bonded C-N species. Also, as shown in the Figure 3(b), the sheet resistance was increased from 400 ohm/sq to 1,300 ohm/sg with increasing oxygen flux up to 100 sccm because surface wettability was increased by increasing oxygen flux during oxygen APP treatment. In the all cases, sheet resistance of CNTs on PI is the lowest even CNTs loaded on both PET and glass is the lowest. It is because of tendency of remaining elongated structure rather than curved structure, which is seen in CNTs morphology on PET and glass substrates that are insulators. This indicates plasma activated ion species as well as electrons with radicals can highly propagates on both CNTs surface and conducting PI surface than those of insulating substrates, resulting in more elongated CNTs structure formation on PI substrate. The lowest sheet resistances of CNTs dispersed on PI and PET were 400 ohm/sq and 550 ohm/sq, respectively.
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ohm/sq, respectively.

Figure 4 shows the SEM images, which show morphology of microwave treated CNT dispersion. CNT dispersion density on PET was decreased with increasing microwave treatment time. Also, curved structure of CNT was changed to elongated structure. We could expect that microwave treated sample with 15 sec has lower sheet resistance than untreated PET sample. This means that CNT dispersion can be changed by either plasma treatment or dispersion time within microwave treatment.

Conclusions

In this work, the electrical property of CNTs loaded substrate and dispersion density on CNTs on each substrate were evaluated using the results of sheet resistance and SEM study. The flowing conclusions were drawn:

(1) Each substrate has different wettability. Also, it was controlled by plasma treatment. PET surface has low water contact angle and weak CHx IR peak.

(2) CNT amount on substrate was influenced by different plasma chemistry and wettability. Density of CNT dispersion is different because substrate has difference surface energy.

(3) Density of CNT dispersion can be changed by plasma treatment of substrate or dispersion time within microwave treatment.

(4) Oxygen or nitrogen APP treatments on substrate lead to increase in sheet resistance.

(5) The sheet resistance for nitrogen APP treated CNTs is higher than that of oxygen APP treated CNTs.

(6) Microwave treatment on CNTs solution decreased the density of CNT dispersion. Also, it gives directivity on CNT dispersion.

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References