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Functionalization of Multiwall Carbon Nanotubes with Atmospheric Dielectric Barrier Discharge for Polymer Composites

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We investigated the effect of dielectric barrier discharge (DBD) onto multiwall carbon nanotubes (MW-CNTs) that are composed into a polymer. The mechanical property of the composited polymer should be changed by both CNTs themselves (physical aspect) and functional groups (chemical aspect). Here, we exposed the discharge made with oxygen and nitrogen gases at atmospheric pressure over the CNTs to functionalize isocyanate group (R-N=C=O). Our preliminary results showed that the wearing rate of the polyurethane film containing the MWCNTs that was exposed with the discharge was smaller than the wearing rate of the polyurethane film containing pristine MWCNTs.

1. Introduction

Carbon nanotubes (CNTs) have been attractive due to the mechanical and electrical properties. However, CNTs are widely known as one of inert materials so that it is not so easy to have a good dispersion in a solvent. A common technique to disperse CNTs is to functionalize CNTs with carboxyl group (-COOH) with strong acid, *e.g.* sulfuric and nitric acid at high temperature. Once CNTs are functionalized, the -COOH groups are replaced with other functional groups so that the CNTs can be treated better.

CNTs are sometimes composited in an organic polymer to compensate the mechanical property of the polymer. Organic polymers have enough flexibility to form, while there is generally a drawback that is poor mechanical properties. Polyurethane (PU) is one of the polymers that have such a typical property. PU is made by chemical reactions with isocyanate (R-NCO) and polyol. Isocyanate plays a role to give the hardness and polyol does to give the flexibility for the polyurethane.[1]

In this proceeding, we will show the results that we were able to attach isocyanate groups on CNTs though plasma. And then, the attached group possibly improved the mechanical property of polyurethane film (PU), in particular, wearing property of PU film. Our result showed that the degree of the improvement in wearing property depended upon the plasma-processing gas.

2. Experimental Setup

2.1 *Plasma Treatment over CNTs*

We functionalized multi-walled CNTs (MWCNTs; Jeio, M-951; 10 – 30 nm dia.) with a homemade dielectric barrier discharge (DBD) at atmospheric pressure. The discharge was created with alternative current at 10 kHz and 10 kV_{pp} in a quartz tube (Labotec, OD: 30 mm, length: 200 mm). The operating power was ~50 watts. Here, we used argon, oxygen, nitrogen, and these mixture gases as the plasma-processing gas. The discharge was created in a closed environment so that no gas flowed during the discharge. The processing gas was selected depending on the purpose of the experiment. The CNTs were exposed in the plasma for 15 to 30 minutes. We also set up a heater at the bottom so that there is an ability to increase the temperature to enhance the chemical reaction.

2.2 *Investigation of Functional Groups on CNTs*

We examined the functionalized CNTs with Fourier transform infrared spectroscopy (FTIR; Perking-Elmer Instruments, Spectrum One) with attenuated total reflectance (ATR) mode in order to find the functional groups on the nanotubes. The IR absorption was taken with 2 to 10 mg of CNTs in the range of 700 to 4000 cm^{-1}.

2.3 *Mechanical Property Test*

Once functionalizing CNTs, we mixed the CNTs into a film that was made by drying PU solution (Miractran, GY-20Z-380) at ambient air for overnight. After the plasma treatment, the CNTs were dispersed in tetrahydrofuran (THF, C_4H_8O; Wako, 109-99-9) solvent with ultrasonication (As-One, ASU-2M) at 60 °C for 60 minutes. After the sonication, we centrifuged the solution with 900 G. Here, we used only the solvent where CNTs were dispersing (*i.e.* not sedimentary part)

when making a PU film.

The thickness of PU film was controlled at approximately 100 μm. The film was cut into 2 mm × 30 mm in order to proceed the measurement of wearing rate. Then, the film was placed on a sand paper to measure the wearing rate of the film. The cut film was attached with 20 g of weight at one side and was fixed at the other side. The wearing rate is defined as the following equation.

$$WR = t / T \quad (1)$$

where *WR* is wearing rate of the polymer film [m/sec.], *t* is film thickness [m], and *T* is the time to tear the film [sec.]

3. Experimental Results

3.1 *IR Measurements*

Fig.1 shows FTIR spectrum when MWCNTs were functionalized with nitrogen and oxygen plasma at several 10 °C. Here, we set the ratio of gas mixture at 50 % for each gas. The transmittance in the figure was normalized with the noise level set at 1. As seen in the figure, a relatively strong absorption peak was observed at 2240 cm^{-1}. The intensity was five times more than noise. According to the gas composition of the plasma and the wavenumber at the peak[2], this measurement indicated that isocyanate groups were attracted on the CNTs though the plasma treatment.

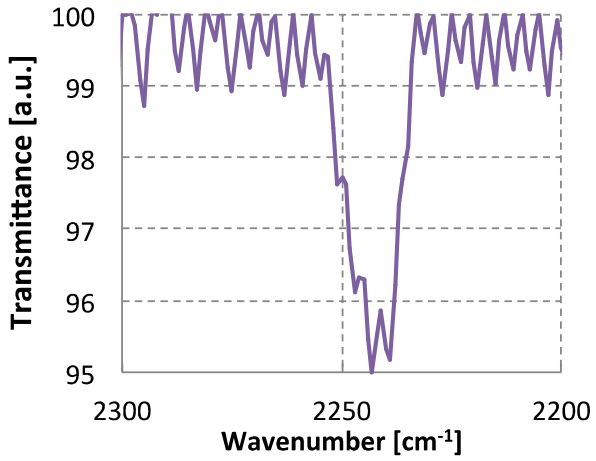

Fig.1. FTIR spectrum of CNTs that were treated with N_2/O_2 plasma.

3.2 *Wearing Property*

Fig. 2 shows the wearing rate for the PU film that contains 1) pristine CNTs and 2) the CNTs treated with N_2/O_2 plasma. Here, we used the THF solvent dispersing CNTs with the concentration at 17 mg/L so that the amount of CNTs in the PU film is approximately 0.02 wt. %. As seen in the figure, the wearing rate of the film composited with plasma-treated CNTs became 3 times smaller than that with pristine CNTs. Note that the smaller wearing rate gets, more anti-wearing property the film has.

As a reason to increase the wearing property of the PU film, we are currently speculating that the isocyanate on the CNTs helped the increase. This is because the wearing rate decreases, in particular, when CNTs were treated with the plasma created with N_2/O_2 mixture. Considering the ratio, the isocyanate can be a good candidate to increase the property.

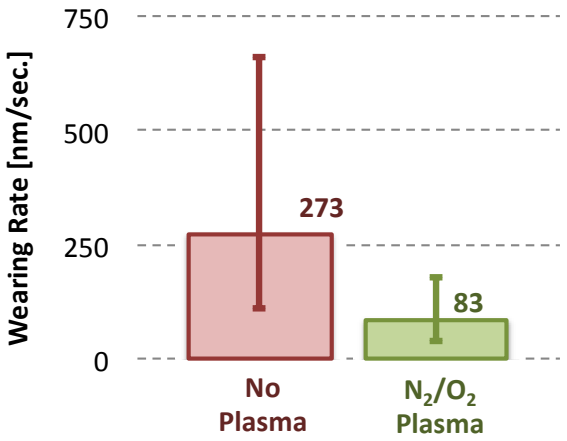

Fig.2. Comparison of wearing rates for the PU film contains 1) pristine CNTs and 2) CNTs treated with N_2/O_2 plasma.

4. Conclusion

From the set of experiments shown above, we were able to attach the isocyanate groups on the CNTs through N_2/O_2 plasma. The attached group also increased the anti-wearing property of PU film. However, we still need to keep our eyes on this result because amount to the functional group of isocyanate is still unknown.

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References

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[2] M.Hesse, H.Meier, and B.Zeeh: *Spectroscopic Methods in Organic Chemistry 2nd Edition* (Thieme, New York, 2007).