Preliminary investigation of boron nitride nanotubes as an active material of sunblock

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Abstract. Boron nitride nanotubes (BNNTs) are investigated as an active material of sunblock. Both the optical calculations and the experimental measurements are performed in this present study. Optical calculation such as the dielectric function of BNNTs are calculated using the random phase approximation (RPA). While, the experimental measurements started with the preparation of sunblock gel samples containing BNNTs with a basic formula consisting of a mixture of carbopol 940 and triethanolamine (TEA). Then, the sunblock gel samples are examined using the UV absorption spectroscopy and the diffuse reflectance spectroscopy. Both the results of the optical calculations and the experimental measurements, show that BNNTs have good absorption in the ultraviolet region and good transparency in the visible light region. This preliminary investigation indicates that BNNTs has the opportunity to be further developed as an active sunblock material.

1. Introduction

Sunblock is a part of skin care products that protects the skin from ultraviolet exposure. Using sunblock on the skin surface is the same as build up layers on the skin surface, functioning as a barrier to the skin from the UV radiation. Generally, sunblock contains inorganic filter as an active material for providing a protection against the UV radiation. Inorganic filter such as titanium dioxide is currently being used as an active sunblock material because it is stable when exposed to the UV radiation, it does not cause damage to the epidermal cells, and it is low allergenicity. Furthermore, titanium dioxide provide a wide spectrum protection including ultraviolet type A (UVA) and ultraviolet type B (UVB) [1–4].

However, the application of titanium dioxide as an active sunblock material which is a part of cosmetics product, have a fateful aesthetic weakness. The high refractive index of titanium dioxide (2.4) may display a particularly white appearance on the skin face because of the light reflection mechanism [5, 6]. An opaque titanium dioxide makes the product is not attractive to consumers [3]. One way to solve this issue is to reduce the size of titanium dioxide grains from (220-250 nm) to 20 nm or less. The particle size significantly affects the level of absorption and reflection of titanium dioxide in the UV region [7]. However, other issues occur as the size of the particles decreases, TiO2 becomes photo-reactive and creates free radicals such as reactive oxygen species (ROS) [7]. ROS is very harmful because it causes skin cancer. Due to the weaknesses of titanium dioxide as an active sunblock material, this encourages the desire to look for other inorganic materials that can improve
these weaknesses. One of the inorganic materials to be tested as an active ingredient in sunscreen is boron and nitrogen based material such as BNNTs.

BNNTs have a similar structure to carbon nanotubes (CNTs) [8, 9], but some of the characteristics of BNNTs are much different from the characteristics of CNTs. BNNTs are an insulator with a wide band gap (5 eV-6 eV) [10–14] which regardless of their geometry, while CNTs are semimetallic and semiconducting material [15–17]. Some of the characteristics possessed by BNNTs are stated to be superior to CNTs, such as BNNTs were predicted to be thermo-mechanically stable at higher temperature [18, 19] and have a higher resistance to oxidation than CNTs [20, 21]. In this case, BNNTs are also expected to be better than TiO2 as a sunblock active material, because BNNTs are transparent and very thermally and chemically stable. Furthermore, the size of BNNTs in nanometer does not make BNNTs become free radicals.

Therefore, this study is aimed to investigate the use of BNNTs as a sunblock active material through both the computational study and the experimental study. The computational study is performed using the density functional theory (DFT) and the random phase approximation (RPA) to get the basic theory of BNNTs optical properties. The experimental work is then carried out by formulating BNNTs into a sunblock gel. This work is expected to be able to prove that BNNTs have the opportunity to be applied to sunblock and are eligible for further investigations.

2. Methods

2.1. Optical Calculation

Optical calculations such as the dielectric function of BNNTs are calculated using the random phase approximation (RPA). The calculations of the RPA will produce a dielectric function consisted of a real part and an imaginary part ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), each of the parts will interpret the refractive index and the absorption of BNNTs. In addition, the RPA needs the initial input such as ground state calculations of Kohn-Sham which calculated using the density functional theory (DFT). The local density approximation (LDA) is applied as an exchange correlation energy [22] and the ultra-soft pseudopotential is used to simplify the interactions between ions-electrons around the cores [23, 24]. The ground state calculations using DFT will stop automatically when it has reached the convergence of the energy difference of $10^{-6}$ eV and the Hellman-Feyman force of $10^{-2}$ eV.

2.2. Experimental Details

2.2.1. Preparation of Samples (Sunblock Gel).

In the present experiment, BNNTs with purify > 90% are applied as an active material of sunblock. First, we need a basic gel formula to make the sunblock gel containing BNNTs. A basic gel that contains water, carbopol 940 as a cosmetic excipient gel and 50% triethanolamine (w/w) as regulator of pH (5-7). The percentages of each component are presented in Table 1. The composition as shown in Table 1 which containing carbopol 940 1% w/w and TEA 1.5% w/w is a stable basic formula based on the parameters of viscosity, spread ability, homogeneity, type of emulsion, pH, and organoleptic [25].

Second, BNNTs are mixed into basic gel formula and then stirred until a homogeneous mixture is obtained. The concentration of BNNTs varies with carbopol 940 (1% w/w) in 100% w/w of basic gel formula, so that four samples are obtained as shown in Table 2.

| Table 1. Gel basic formula composition |
|---------------------------------------|
|            | Aquades (% w/w) | Carbopol 940 (% w/w) | TEA (% w/w) |
| Ad 100     | 1               | 1.5                 |             |
Table 2. The variation of BNNTs concentrations in basic gel formula.

| Sample | BNNT (% w/w) | Basic Gel (carbopol 1% w/w) |
|--------|--------------|-----------------------------|
| 1      | 0.25         | 100                         |
| 2      | 0.5          | 100                         |
| 3      | 0.75         | 100                         |
| 4      | 1            | 100                         |

2.2.2. Characterization. The four samples are physically characterized to get the absorbance and the reflectance of them in the spectra of the ultraviolet and the visible light. Each characterization is detailed as follows:

1) The Absorbance of Sunblock Gel Using UV Absorption Spectroscopy

Measurements are made by applying the sample on a 1 mm thick glass slide as much as 2 mg/cm² using a brush. The samples are allowed to dry and then placed in a UV-vis spectrophotometer. Before measuring the samples, a blank glass slide is measured. Experiments are carried out for the four samples and the spectral data are processed from the lab sphere software where critical wavelengths are calculated.

2) The Reflectance of Sunblock Gel Using Diffuse Reflectance Spectroscopy

A different setting of a UV-vis spectrophotometer is needed to measure the reflectance of the four samples. The location of the light sources and the site of the samples in the reflectance measurement differ from the absorbance measurement. Furthermore, measurement of the reflectance of the four samples using a special container which made of sapphire. Measurement of reflectance is done by inserting the gel into a container and then placed into a UV-vis spectrophotometer. Measuring the reflectance of this sample refers to the results of optical standard MgO measurements in the visible light spectrum with wavelengths of 400 nm - 700 nm.

3. Results and Discussions

3.1. Optical Properties: Dielectric Function

Figure 1 represents the dielectric function of BNNTs with respects to the radiation energy. The dielectric functions of the (5,0) BNNTs and the (5,5) BNNTs are displayed to represent the dielectric function of the other geometry of BNNTs. The optical spectra are divided into infrared (IR) energy range from 0 to 1.7 eV, the visible light (VL) energy range 1.7 eV to 3.3 eV, the ultraviolet (UV) energy range 3.3 eV to 12.4 eV, and the X-ray >12.5 eV as shown in Figure 1. The BNNTs dielectric function consists of the real part (blue line) and the imaginary part (red line). The real part of the BNNTs dielectric function informs the refractive index of BNNTs are 1.18 a.u. for (5,0) BNNTs and 1.2 a.u. for (5,5) BNNTs. While, the imaginary part of the BNNTs dielectric function displays the main absorption peaks of BNNTs are found in the UV region for both (5,0) and (5,5) BNNTs. The main absorption peaks of BNNTs are located in The UV region indicate that BNNTs have ability to absorb the UV radiation.

Since BNNTs are planned to be utilized as a sunblock active material, so the focus of this discussion is the absorption in this UV region. The BNNTs absorption is not affected by BNNTs’ geometry such as chirality, so the absorption peaks of all BNNTs are located in the almost same region of energy. Furthermore, a very low absorption occurred in the visible light region is good, since the BNNTs need to transfer some the visible light to create a transparent sunblock.
3.2. The Absorbance of Sunblock Gel

Figure 2 shows the sunblock containing BNNTs with four variations of concentration in basic gel formula. These four samples indicate the maximum absorbance peaks in the range of UV region. Furthermore, the height of these absorbance peaks is affected by the concentration of BNNT (% w/w) in basic gel formula (carbomer). The increasing concentration of BNNTs in basic gel formula increases the absorbance peak of the sample.

The sample 1 containing 0.25% w/w of BNNTs has a ramp absorbance peak at 0.125 a.u. When the BNNTs concentration increase to 0.5% w/w (sample 2), its absorbance peak shift up to 0.175 a.u. This increasing of the absorbance peaks pattern is not linear when the BNNTs concentrations are increased to three and four times higher than the concentration of BNNTs in the sample 1 as illustrated in Figure 2. However, we can conclude that the sample 4 with 1% w/w of BNNTs concentration in basic gel formula is the best sample among the others because it has the highest absorbance.

3.3. The Reflectance of Sunblock Gel

The reflectance of the four samples of the sunblock gel containing BNNTs is shown in Figure 3. Based on the Figure 3, we conclude that the reflectance of the four samples is not influenced by the BNNTs concentration in basic gel formula. The four samples indicate the similar percentage of reflectance in the range 300 nm — 800 nm of wavelength. The percentages of the reflectance of the four samples are quite low in the range UV and the visible light region (50%), but these percentages will increase to the infrared region. The increasing the samples’ reflectance in the infrared region indicates that BNNTs has a low transparent in that region.
3.4. The Correlation Between Optical Calculation Results and Experimental Measurements

The correlations between optical calculation results and experimental measurement outcomes are quite strong. The imaginary part of the dielectric function of BNNT and the absorbance measurement of the sunblock gel, indicates that BNNTs have the main absorption peaks in the UV region. This finding means that the sunblock gel containing BNNTs can absorb the UV radiation.

Furthermore, transparency of sunblock gels containing BNNTs needs to be discussed. The transparency around the visible light region is needed to display the natural skin tone. This transparency is shown by the imaginary part of the BNNTs dielectric function which states that there are no absorption peaks exhibit in the visible light region. Then, the reflectance measurement of the four sunblock samples represents that BNNTs reflects 50% to 60% of the visible light. It shows that BNNTs is quite transparent with 40% until 50% transmission of the visible light.

Figure 2. The absorbance of sunblock gel with 4 variations of BNNTs concentration (% w/w) in basic gel formula (carbomer).
Figure 3. The reflectance of sunblock gel with 4 variations of BNNTs concentration (% w/w) in basic gel formula (carbomer).
4. Conclusion

In summary, the optical calculations and the experimental measurements have been completed as a preliminary study for investigating a sunblock containing BNNTs. The four samples of the sunblock gel containing BNNTs have the absorption activity in the UV region. The concentration of BNNT (% w/w) in basic gel formula (carbomer) influences the height of the absorption peaks. While, these BNNTs concentrations do not affect the reflectance percentages of the four samples. In this present study, the BNNTs with 1% w/w of concentration in basic gel formula are concluded as the best sample because of its highest absorption peak in the UV region among the other samples. It is also quite transparent in the visible light region, which in terms of aesthetics is interesting. Based on these results, a sunblock gel containing BNNTs as an active material, has the opportunity to be further developed in the future with further testing.

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