Short Communication

Protecting Surfaces Using One-Dimensional Nanostructures

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Abstract:
Ultraviolet waves, because of their short wavelength, have a high energy and considerable damaging effects on surfaces. Protection against ultraviolet radiations is one of the finishing treatments done on surfaces exposed to sunlight. The importance of this issue in relation to human health, due to complications such as skin burns and cancer, is doubled. Up to now, different materials such as zinc oxide, titanium oxide and Aluminum oxide nano-particles have been introduced as the ultraviolet absorbents. In this paper, the absorption of single-walled carbon nano-tubes (SWCNTs) and multi-walled carbon nano-tubes (MWCNTs) was investigated and compared with common chemical absorbent materials. The results showed that carbon nano-tubes (CNTs), similar to other absorbents, have a specific absorption in this area. In addition, it was observed that the absorption of SWCNTs is comparable with other absorbents, and CNTs could be introduced as good substitutes for ultraviolet absorbents in various applications.
Keywords: *Nano-particles, Single-walled carbon nano-tubes, Multi-walled carbon nano-tubes, Ultraviolet radiation, Absorption.*

1. INTRODUCTION

Ultraviolet radiant of the sun's spectrum is not visible to human. Based on a classification, wavelength region of the solar spectrum is divided into three parts, A (390-320), B (320-280), C (280-220) nm. This radiant, because of short wavelength, has high energy [1]. Coatings and surfaces are inevitably exposed to the destructive effects of this range of radiation.

On the other hand, the importance of this matter to human health, due to complications such as skin burns and skin cancer, is doubled [2]. Today, in order to increase efficiency and productivity, many additional operations on the cover are done ,such as automotive coatings, military equipment, canopy, textiles, etc. [3].

One of these finishing treatments is protecting against ultraviolet radiations. Normally, for this type of treatment, chemical ultraviolet absorbers are used. The energy of ultraviolet photons reaching Earth's surface is about 235 kJ/mole, which equals the energy of the carbon double bond linkage. So these absorbents have many carbon double bonds in their molecular structure, such as benzotriazoles [4]. With the advent of mineral particles, many successful efforts to create new properties in the composite by adding nano-particles have been made. Using inorganic nano-particles in polymeric composites, one can simultaneously obtain several properties such as strength, chemical and thermal resistance, hydrophobic and hydrophilic, anti-abrasion and anti-fire, which are much less expensive than conventional materials [5].

The nano-particles of titanium dioxide, zinc oxide and aluminum oxide, which are also called photo catalytic nano-particles, are used in order to protect against ultraviolet radiates [6].

By discovery of carbon nano tubes in 1991 by a Japanese scientist named Iijima, a new window was opened for science. Carbon nano tubes are one-dimensional nanostructures. They are of two types: single-walled and multi-walled with the former having higher purity. These nano-particles, in terms of structure, are divided in two types of metal and semiconductor. The general properties of carbon nano tubes are high Young's modulus, high thermal and electrical conductivity due to high aspect ratio, excellent thermal stability and chemical storage of hydrogen and helium and others [7].

By adding carbon nano tubes to polymers, many of its properties were modified. So today they are one of the best fillers to polymeric composites [8]. In addition, by using a very small percentage of the CNT, other unique properties such as antifire, Lotus effect, anti-static, anti scratches enhanced mechanical properties [9]. In fact, by treating the surfaces with CNTs, multi-functional surfaces can be achieved.

For example, using this nano-tube can produce unique protective clothes that are used as firefighters clothing, army forces in wartime, workers in sensitive areas, etc. [1]. In addition, with finishing surfaces such as car coverage, using these nano-particles, its metal and paint corrosion, which is the result of sunlight exposure, is prevented. Also, if CNTs covered the surface as arrays, their absorption would be greatly increased. In this case, these surfaces can also be used as plates of solar battery [10].

In this paper, the ability of nano tubes to absorb ultraviolet radiation was studied and the absorption of these materials was compared with that of conventional ultraviolet absorbers, such as zinc oxide and titanium dioxide at the size of nano and micro, and with the conventional chemical absorbent.

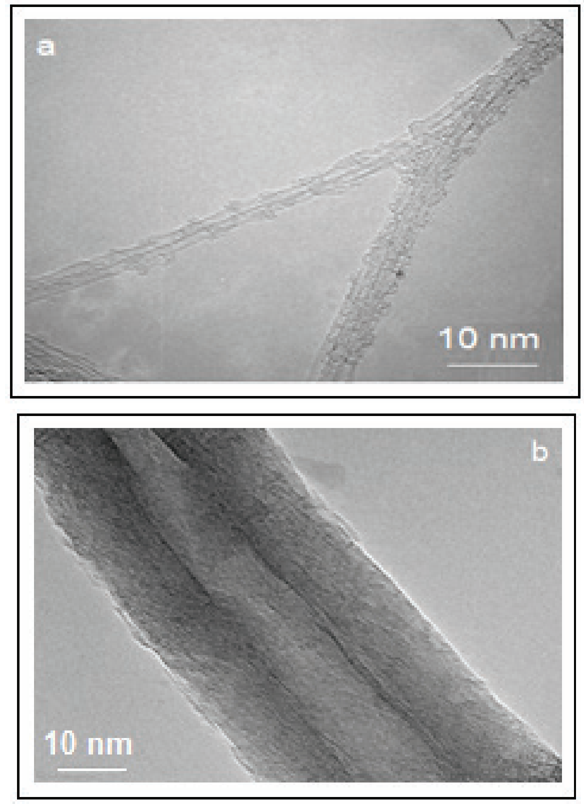

Figure 1: *Scanning electron microscope (SEM) of (a) SWCNT (b) MWCNT*

In order to compare the absorption behavior of the single-walled and multi-walled carbon nano tubes, highly uniform and homogeneous solutions with definite concentration of both types of carbon nano tubes were prepared, and their absorption spectrum, obtained by spectrophotometer, was compared. In order to study the functional efficiency of carbon nano tubes in the protection against ultraviolet radiation, cotton fabric as a representative was selected and carbon nano tubes by conventional resins, used in textile printing, were represented on the fabrics.

The results showed that carbon nano tubes, such as ultraviolet absorbents, are used, having a specific absorption in the ultraviolet region. In addition, it was observed that the absorption of carbon nano tubes, as compared with other sorbent materials, are significantly more attractive, and can be as an alternative to more conventional high-performance ones.

2. METHOD

Nano and micro scales of Titanium dioxide and zinc oxide, sodiumdodecylsulfate (SDS) surface active agent and two multi-walled carbon nanotubes with a diameter of 50 nm (from Merck, Germany) single-walled carbon nanotubes with a diameter of about 1 nm (petroleum research institute), chemical absorbent CIBA FAST W (CIBA, Germany) were purchased. For testing on the fabric, 100% cotton fabric and 100% wool fabric were used. Basic dye 9 (methylene blue) and acetic acid were used for dyeing woolen clothe substrate.

3. EXPERIMENTAL

Since the type of solvent used for dispersion and the amount of it influence the absorption amount of material, the absorption of nano and micro powder particles and liquid chemical UV absorbers were studied. Thus, samples were ground to fine powder particles to accumulate particles in any of them, which might disappear, and obtain a uniform powder.

The absorption rate was measured by the photo luminance and results were plotted as a graph. To study and compare the absorption amount of SWCNT and MWCNT, a uniform dispersion of both with a concentration of 3 mg/ml in 2% solution of SDS was prepared [11, 12]. The dispersion was ready by adding 0.15 g carbon nano tubes dissolved in 50 ml of 2% SDS solution and was exposed to ultrasound for 5 hours with a cycle duty of 70% and a very stable and non-cumulative dispersion.

For this purpose, Sodiumdodecylsulfate was used as a surfactant. This surfactant with surrounding CNTs creates negative charge at the surface and desorbing forces between CNTs, making dispersion was possible. The absorption of dispersion was studied with UV-VIS spectrophotometers, and absorption spectra were prepared.

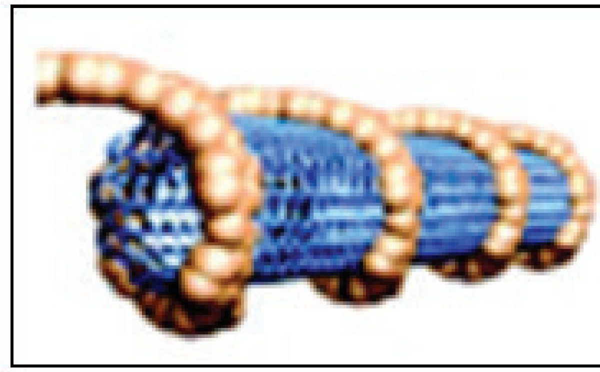

Figure 2: *Application of SDS in CNT dispersion*

Due to high humidity absorption and the breathability properties of cotton fabrics, these types of textiles are used in the summer too. Sun's position in this season makes the ultraviolet radiations reach Earth's surface higher than other seasons.

So the cotton fabrics were chosen as represented surface was exposed to ultraviolet radiation to study the absorption behavior of carbon nanotubes. To study the absorption rate of sorbents applied on cotton fabric, a colored woolen fabric was placed under cotton fabrics.

Thus, colored woolen fabric, dyed with methylene blue with very low light stability (light stability around 1), was placed under cotton fabric treated with UV absorbents. It was exposed to ultraviolet radiations produced by the Sun Test (Zenotest). The amount of Pallor of woolen fabric samples was evaluated.

To prepare the woolen fabric, the samples were woven with 100% woolen yarn, dyed with 1% solution of basic blue 9 (methylene blue) as well as 1% acetic acid at 80 °C for one hour [13]. To prepare cotton fabrics treated with absorbents, 4% and 8% solutions of multi-walled carbon nano tubes were added to the common acrylated resin used in textiles pigment printing.

Then composition of absorbent materials in the resin was placed on the washed and dried cotton fabrics by a laboratory pad machine. To fix the resin, the fabric was dried for 20 minutes at 90 °C to remove hole the water. It was maintained in the oven for 10 minutes at 120 °C. Then, the amount of woolen fabric's color changed as evaluated by colorimeter in gray scale.

RESULTS AND DISCUSSION

As mentioned above, ultraviolet absorbents have many conjugated carbon – carbon linkages in their molecular structure. The carbon-carbon double bond has a peak around 1600 cm^{-1} in IR spectrum [11]. As can be seen in Figure 3, the intensity of the peak in 1600 cm^{-1} and as a result, the amount of these double bonds in CNTs is more than other materials.

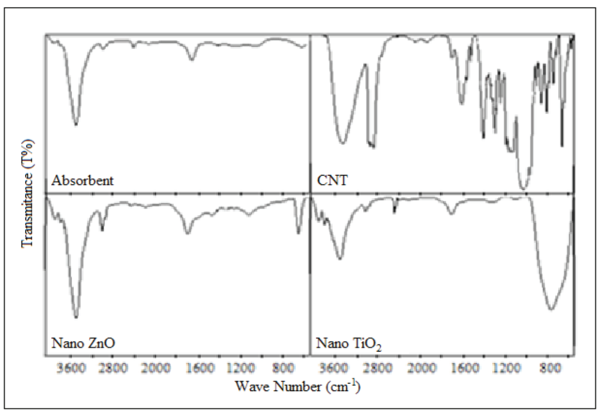

Figure 3: *FTIR of CNT and different absorbent materials*

The absorption curves of nano titanium dioxide, nano zinc oxide, MWCNT and CIBA liquid chemical absorbent (we called it absorbent) were studied. The shape of all the diagrams was plotted in a general graph (Figure 4). To select the best ultraviolet absorbent, we need to introduce a decisive factor.

In this paper, the area under the absorption curve of materials from 200 to 400 nm was plotted and determined as a protection factor for the various materials. Hence, the area under the absorption curve from 200 to 400 nm is shown as a bar graph in Figure 4.

As can be seen in Figure 4, except CIBA absorbent that has an absorption peak in the UVA, the rest of the materials are absorbed in the UVB, showing that common chemical ultraviolet absorbent is not by itself capable of protecting the surfaces. By combining them with the nano-particles, they can be completely covered both UVB and UVA regions.

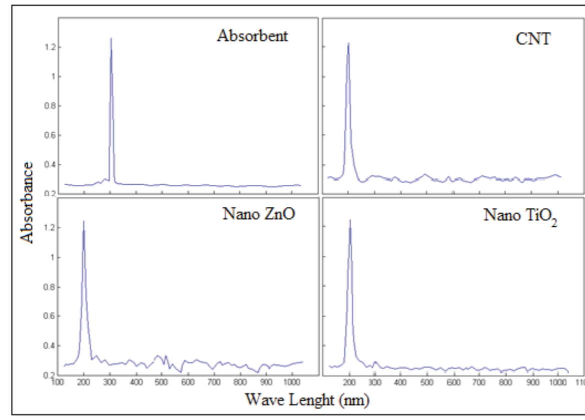

Figure 4: *Absorption curves of different absorbent materials (with UV-visible spectrophotometer)*

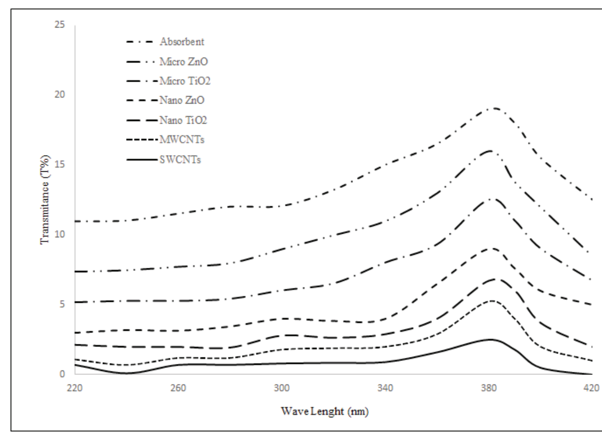

Figure 5: *UV radiation transmittance curves of different absorbent materials*

Figure 5 displays the transmittance of UV radiations through treated cotton fabrics with the different UV absorbents. The results show that the amount of UV transmitted through SWCNTs and MWCNTs are lower than the other absorbents .Also micro TiO_2 and micro ZnO more than nano TiO_2 and nano ZnO transmitted the UV Radiations.

As can be seen in Figure 6, the protection of CNTs is further compared with other materials, showing the ability of these nano-particles in removing ultraviolet radiations. Generally, when the surfaces of different particles are exposed to electromagnetic waves, if the wavelength amount of the magnetic equals its band gap, the wavelength to be absorbed causes valance electrons of the particle layer to be transmitted to the conduction layer; thus, a hole and an excited electron are formed in the atoms of material [6]. Figure 7 is a schematic of the photo catalytic materials against the ultraviolet rays.

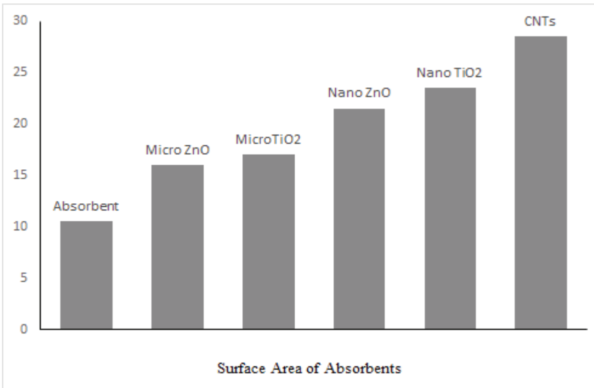

Figure 6: *Protection amounts of different absorbents*

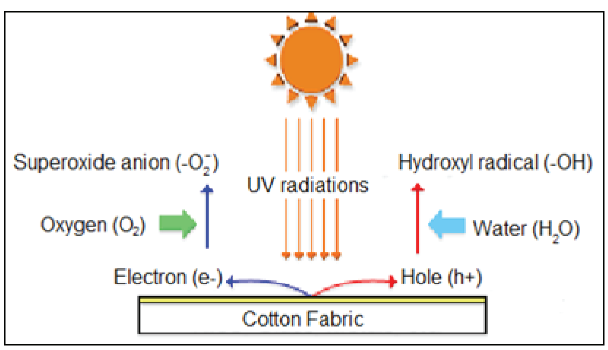

Figure 7: *Photo catalytic materials behavior against the ultraviolet rays*

In titanium dioxide and zinc oxide nano-particles, the energy of band gap is 3.6 and 3.4 electron volts, respectively, the same as the energy of ultraviolet wavelengths. This is a factor justifying the absorption of ultraviolet radiations by these particles [6]. But the amount of this energy for CNTs is about 50-10 electron volts, which is not the same with ultraviolet radiation wavelength [1]. Figure 7 shows the photo catalytic behavior of these particles products radicals in which pollution breaks and the surface has antibacterial, anti-odor, and self-cleaning properties; but there is no report to suggest that the CNTs have this ability.
So this is another factor causing such an attractive behavior of CNTs. According to the conducted surveys, there is a possibility that after the waves hit the CNTs, their energy is lost and trapped inside the hollow structure of nano tubes and finally, absorbed. It should be noted that in semiconductor SWNTs, the photo luminance phenomenon occurs and this phenomenon was not observed in MWCNTs [14]. This means that the SWCNT's electrons were transferred to the higher layers of atoms with the absorption of the ultraviolet radiant.
Also, with transferring back to the first-mode waves with a length of higher shortwave ultraviolet, they emit their own [15]. By studying the absorption ratio of SWCNTs and MWCNTs solutions, it became clear that the absorption intensity of SWCNTs is much higher than MWCNTs, showing the higher purity of SWCNTS towards MWCNTs. On the other hand, the diameter of SWCNTs approximately is 1.50 times more than MWCNTs. At a certain concentration of both types, the number of SWCNTs is much more than the other types. So the absorption ratio of SWCNTs is more.
Because there are the SWCNTs with a mixture of 30% metallic and 70% semi conductive, the photo luminance phenomenon occurs in semi-conductor type, causing more absorption of SWCNTs [7, 14]. Absorption spectra of SWCNTs and MWCNTs are shown at Figure 8.

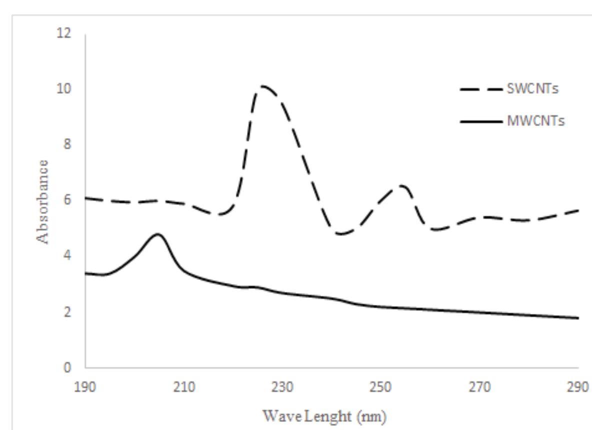

Figure 8: *Absorption spectra of SWCNTs and MWCNTs*

To review and compare the results of woolen fabrics, the gray scale was used. To calculate this scale, the color differences between the woolen samples placed under the cotton fabrics, which, in turn, were treated with chemical absorbent, were compared.

Results are shown in Table 1. As can be seen from Table 1, with increasing the percentage of CNTs and chemical absorbents, the gray scale is closer to the number 5 (color difference between the unexposed woolen samples with exposed samples can be seen below). On the other hand, the gray scale of CNTs in all cases is higher than the chemical absorbent, showing the higher ability of CNTs to protect against ultraviolet radiation.

Table 1: *Gray scale of woolen fabrics placed under treated cotton fabrics*

Woolen fabric	Gray scale
Just with resin	2.4
4% CNT	3.5
8% CNT	3.9
4% chemical absorbent	3.1
8% chemical absorbent	3.4
Uncovered	1.6

4. CONCLUSION

In this paper, the ability of ultraviolet radiation absorption of SWCNTs and MWCNTs was studied. It was found that the amount of ultraviolet radiation absorbed by these particles was much greater than the other conventional materials used. They can be, therefore, a superior alternative.

When radiations hit the CNTs, confinement within their hollow structure and ultimately, the energy loss after consecutive collisions with the walls are recommended as the main factor in the absorption by CNTs.

Color Changes of woolen fabrics under cotton fabrics exposed to ultraviolet radiation were evaluated. It was observed that absorption of CNTs was higher than the chemical absorbents. The absorption peak of the chemical common absorbents was observed in the region of UVA.

By mixing the adsorbent with CNTs, the whole range of ultraviolet waves exposed to earth was completely covered, achieving full protecting. In addition, the negative effects of CNTs' Color were reduced.

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