Effect of Laser on Carbon nano-tubes /Poly vinylalcohol Composite used in Microwave Shielding

Gamal M. Nasr [1], Ashraf S. AbdelHaleem [2], AnkeKlingner[3], Adel M. Alnozahy[4], MagdyMorad[4]

[1] Physics Department, Faculty of Science, Cairo University, Egypt
[2] Armed forces, Egypt
[3] Department of Physics, Basic Science, German University in Cairo, Egypt.
[4] National Institute of Laser Enhanced Sciences, Egypt
ashraf_20091@hotmail.com; hannshawky@yahoo.com

Abstract: Poly (vinyl alcohol) (PVA) / sodium dodecyl sulfate (SDS) / carbon nanofiller (CNT) camposite with various CNT contents (up to volume fraction(V)= 0.038) were fabricated and irradiated with different doses of laser (up to 200 Joules), their dielectric properties were evaluated, and their microwave absorption properties were evaluated. The uniform, stable dispersion and well oriented CNT within the PVA matrix were achieved through using SDS as dispersing agent. The dielectric analysis of the PVA/CNT samples irradiated with laser revealed that the percolation threshold was appreciably changes from 0.019 to 0.029 by laser beam energies up to 200 Joule. It was observed that absorption microwave properties improved with increasing in the loading levels of CNT (up to V= 0.038) as well as laser energy (up to 200 Joules). The maximum value (129.5dB) of the SE_T is obtained at (36.5GHz) for the composites with V= 0.038 after exposed to (200 Joules) of laser beam. From our results we can conclude that, by using Sohi et al model, one could interpret the change in the percolation threshold owing to the change of the geometric factor that defines the geometry arrangement of conductive chains and their overlap in the PVA matrix. The skin depth decreases with the increasing of CNT (to 0.04 V. fraction) by approximately 400 times its initial value and increases by four-order of magnitude upon irradiated the samples by 200 Joule laser-beam. The maximum value of SE_T (129.5dB) is obtained (at 35 GHz) for the irradiated composite loaded with 0.038.
[Gamal M. Nasr, Ashraf S.AbdelHaleem, AnkeKlingner, Adel M. Alnozahy and MagdyMorad. **Effect of Laser on Carbon nano-tubes /Poly vinylalcohol Composite used in Microwave Shielding.** *Life Sci J* 2015;12(3):110-117]. (ISSN:1097-8135). http://www.lifesciencesite.com. 15

Key words: Poly VenylAlcohol, Carbon nanotube,Co_2 laser, Microwave shielding.

1. Introduction

In the last decades laser has become an important tool for material processing at the industry, being mainly used for welding, cutting and drilling[1]. Laser beam is used to induce permanent changes in the surface on the bulk of materials to produce 3-dimension microstructures. Because of the nonlinear nature of the process, the materials modification occurs where the light intensity is high enough, i.e, only in the focal volume. Thus, by moving the sample with respect to the laser focus, it is possible to change the materials properties, such as the refractive index, nonlinear optical susceptibility, crystalline structure and morphology, with high spatial precision[2,3].

2. Experimental

PVA powder (Mw = 72000 g/mol, 98% hydrolyzed) as a polymer was obtained from Merck and CNT (purity = 95%, diameter ~ 8 nm, Length: 30 μm) were supplied from Neutrino Company. Sodium dodecyl sulfate (SDS) was obtained from Sigma-Aldrich. The solvent used for dissolving PVA and PVA/SDS/CNT dispersion was distilled water. All reagents used were of analytical grade and were used as received without further purification.

Preparation of Samples

Solutions were prepared in three steps. First, the solution samples were prepared by dissolving 1wt% SDS in distilled water using magnetic stirrer (corning hot plate stirrer PC-351) at 25 0C for 1 hr. In the second step; different weights of CNT were dispersed in the SDS/H2O solutions byusing a high power ultrasonic homogenizer (UP200, Germany) at 0°C for 20min. 8wt% of PVA in sonicated solutions by using a magnetic stirrer at 80^{0}C for 2hr. The calculated CNTs concentrations in each composition of any sample are listed in Table 1.1.

Laser treatment is performed using a CO2-pulsed laser (Lumonics 103-2) with a pulse duration or full width at half maximum (FWHM) of the applied CO2 laser is about 80 ns in standard room conditions. The pulse width, pulse duration, or FWHM of the applied CO2 laser is about 80 ns, and its tail is about 3–4 ls. The wavelength of CO2-pulsed laser is measured by a CO2-laser spectrum analyzer (Opt.Instru- ment 16-A Nexus) and is set at 9225 nm.

Measurement and Characterization

The dielectric properties was measured using a bridge (type INSTEK –LCR821) in the frequency range of 1- 200,000 Hz. Samples were in the form of

disks of 0.1 cm and 2cm diameter.The microwave-absorbing properties of the composite were investigated using HP Vector Network Analyzer (Model 8510ES) in the frequency range of 1-40 GHz at room temperature.

Table 1: Concentrations of CNT, SDS, and PVA in the mixed solutions

	Mass in 100ml H₂0			CNT
	PVA(mg)	SDS(mg)	CNT(mg)	Mass ratio(wt%)
CNT-0	8000	920	0	0
CNT-1	8000	920	90	1
CNT-2	8000	920	180	2
CNT-4	8000	920	360	4
CNT-6	8000	920	540	6
CNT-8	8000	920	720	8

3. Results and Discussion
1.Dielectric Properties

In this section, we show some results we obtained in the use of laser to dielectric properties as well as microwave shielding properties for our samples.

Ac conductivity calculated at 20 Hz, room temperature (300K) and at different laser beam irradiation energy (0, 50, 100, 150 and 200 Joules) for PVA/ loaded carbon- nano-filler are present in Figure (1).

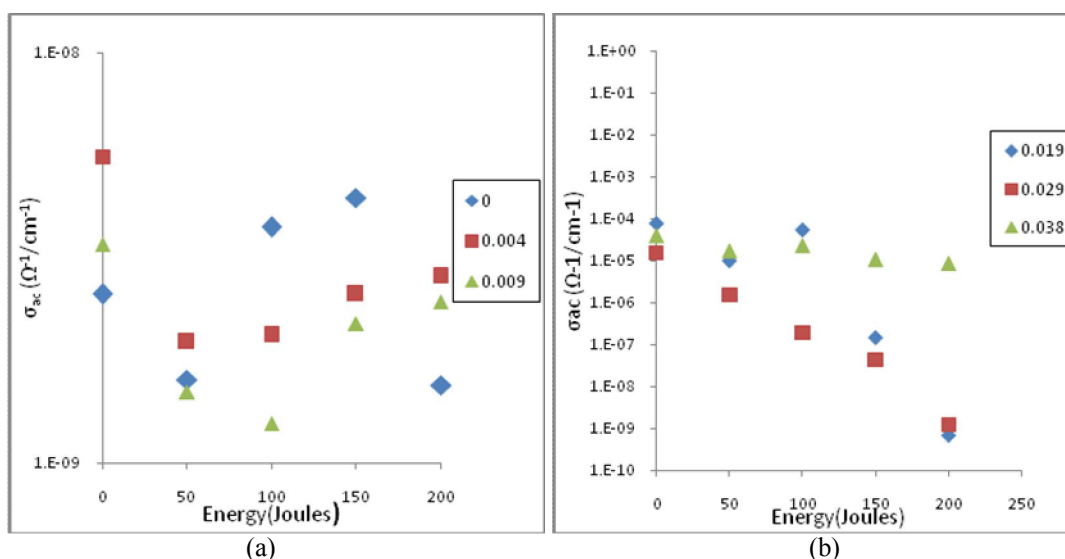(a)   (b)

Figure (1 a-b): ac conductivity calculated at 20 Hz, room temperature (300K) and at different laser beam irradiation energy (0, 50, 100, 150 and 200 Joules) for PVA/ loaded carbon- nanotube

In case of loaded PVA with carbon nanotube contents less than the percolation threshold, one could observe a gradual decrease in σ_{ac} with laser energy up to 100 Joules followed by an abrupt increase till 150 Joules. This may be attributed to the increase of the amount of accumulated charge (due to laser beam) which causes increase in the polarization effects.

PVA/ loaded with higher concentration of carbon nano-tube (0.019<0.029) show an exponential decrease in its σ_{ac} with laser beam energy (up to 200Joules) Meanwhile, PVA samples loaded with 0.038 CNT shows an appreciably independent behavior of its σ_{ac} with laser energy, which reflects the important role of carbon nanotube in the σ_{ac} dependent of laser energy.

Following the dielectric analysis and the power law equation $\acute{\varepsilon} \ (V_c - V)^{-s}$, the critical filler volume fraction V_c and the s exponent of $\acute{\varepsilon}$ are calculated as function of laser beam energy as shown in Table (2) and Figure (2 a – e).

(a)

(b)   (c)
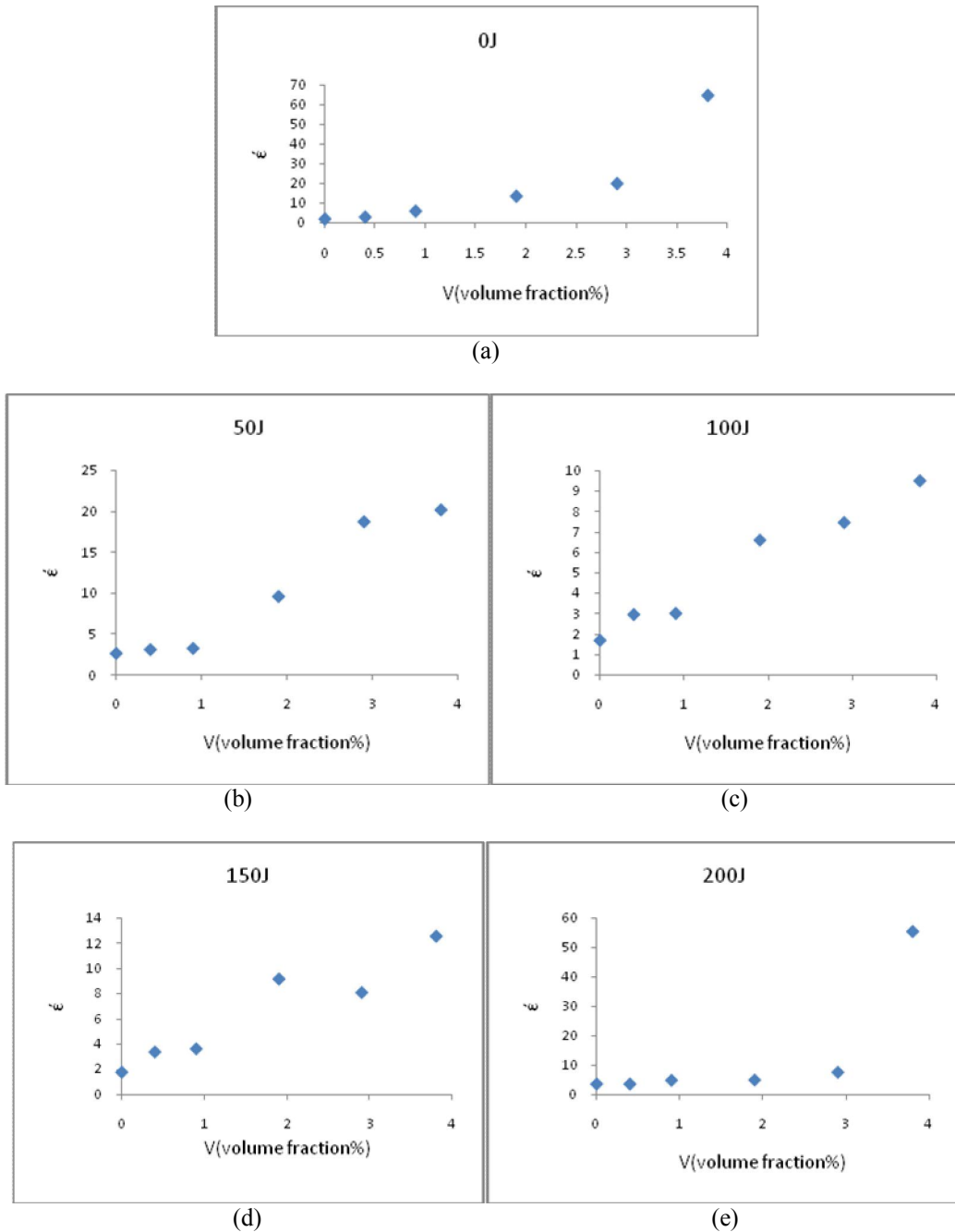

(d)   (e)

Figure (2 a – e): The frequency variation of ἐ at V ~ V_c as predicted by the percolation theory examined at different laser energy.

Table (2): the s exponent of ἐ are calculated as function of laser beam energy

Energy(Joules)	s
0	0.7
50	0.729
100	0.934
150	1.09
200	1.3

The frequency variation of ἐ at V ~ V_c as predicted by the percolation theory given by equation (1) was examined at different laser energy and tabulated in Table (3). Moreover from the plots of the σ_{ac} at V ~ V_c and the frequency one could also calculate the critical exponent u of equation (2) (cf Figure 3).

$$\varepsilon'(\omega, V_c) \; \alpha \; \omega^{-\upsilon} \tag{1}$$

$$\sigma_{ac}(\omega, V_c) \; \alpha \; \omega^{\,u} \tag{2}$$
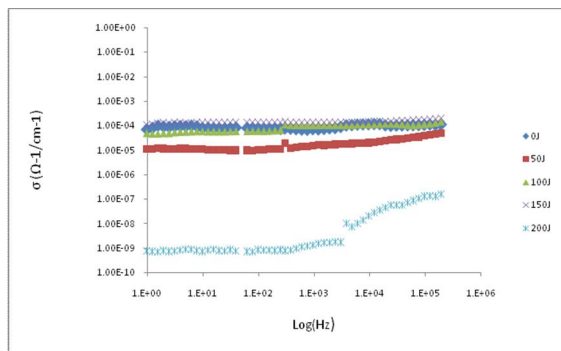
Figure(3): The plots of the σ_{ac} at V ~ V_c and the frequency.

The critical exponents' u and v are shown in Table (3.2) at different laser energies. All exponents satisfy the percolation phenomenon of PVA/ CNT at different laser energies.

Figure (4) represent the σ_{dc} of the composite system as a function of filler concentration at different laser beam energies.

Table (3): The critical exponents' u and v at different laser energies

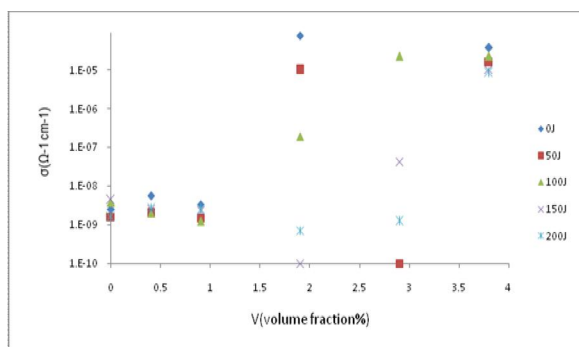| Energy(Joules)	u	v
0	0.0214	0.99
50	0.02	0.98
100	0.019	0.97
150	0.03	0.965
200	0.032	0.968

Figure (4): The σ_{dc} of the composite system as a function of filler concentration at different laser beam energies.

For laser beam energies less than 150 Joules, conductivity of the composites initially increase slowly with increasing the filler (CNT) concentration less than (0.019), followed by a sharp increase in conductivity when the concentration is increased

above (0.019) However, the increase of conductivity is marginal when the concentration of (CNT) is increased beyond (0.019) for all laser beam dose ≤ 100 Joules. Increasing the laser beam energies ≥ 150 Joules, one could observe an appreciable increase in the percolation threshold.

Sohi et al[4] took in their consideration the effect of aspect ratio and surface area to volume ratio of fillers in the formation of conductive network. They suggest a theoretical model to study the effect of filler contents on the electrical conductivity of polymer composites. The equation put forward by Scarisbrick[5] is modified by Sohi et al[4] through the introduction filler aspect ratio, surface area to volume ratio, and conductivity of the polymer. Their proposed model equation is as follows:

$$\sigma_c = C \times \sigma_f \times \frac{A}{10} \times S \times V \times (V)^{\frac{-1}{A}} + (1-V)\sigma_p \quad (3)$$

where σ_c, σ_f, σ_p are the conductivities of composites, filler and polymer, respectively, V is the volume fraction of the conductivity filler in the composite and C is the geometric factor that defines the geometry arrangement of conductive chains and their overlap in the matrix.The value of C varies from 10^{-3} to 10^{-5}, A is the aspect ratio and S is the surface to volume ratio in μm^{-1}, which can be calculated from the shape and size of the fillers. The values of A and S for CNT are A= 5, S= 100μm^{-1}.

The theoretically calculated conductivities using Sohi et al[4] model are very close to the experimentally determined conductivities for all laser irradiated composite systems over both low and high concentrations of filler (cf. Figure 5).

The values of the parameter C that gave better fitting for all irradiated laser composite are given in Table (4). One can notice that C decreases with increasing laser energy > 100 Joules and give account for the increasing percolation threshold. So the arrangement of conductive chains and their overlap in the matrix decreases appreciably with laser irradiation dose.

Table(4): The values of the parameter C that gave better fitting for all irradiated laser composites.

Laser energy (Joules)	C(10^{-6})
0	1000
50	1000
100	20
150	5
200	1
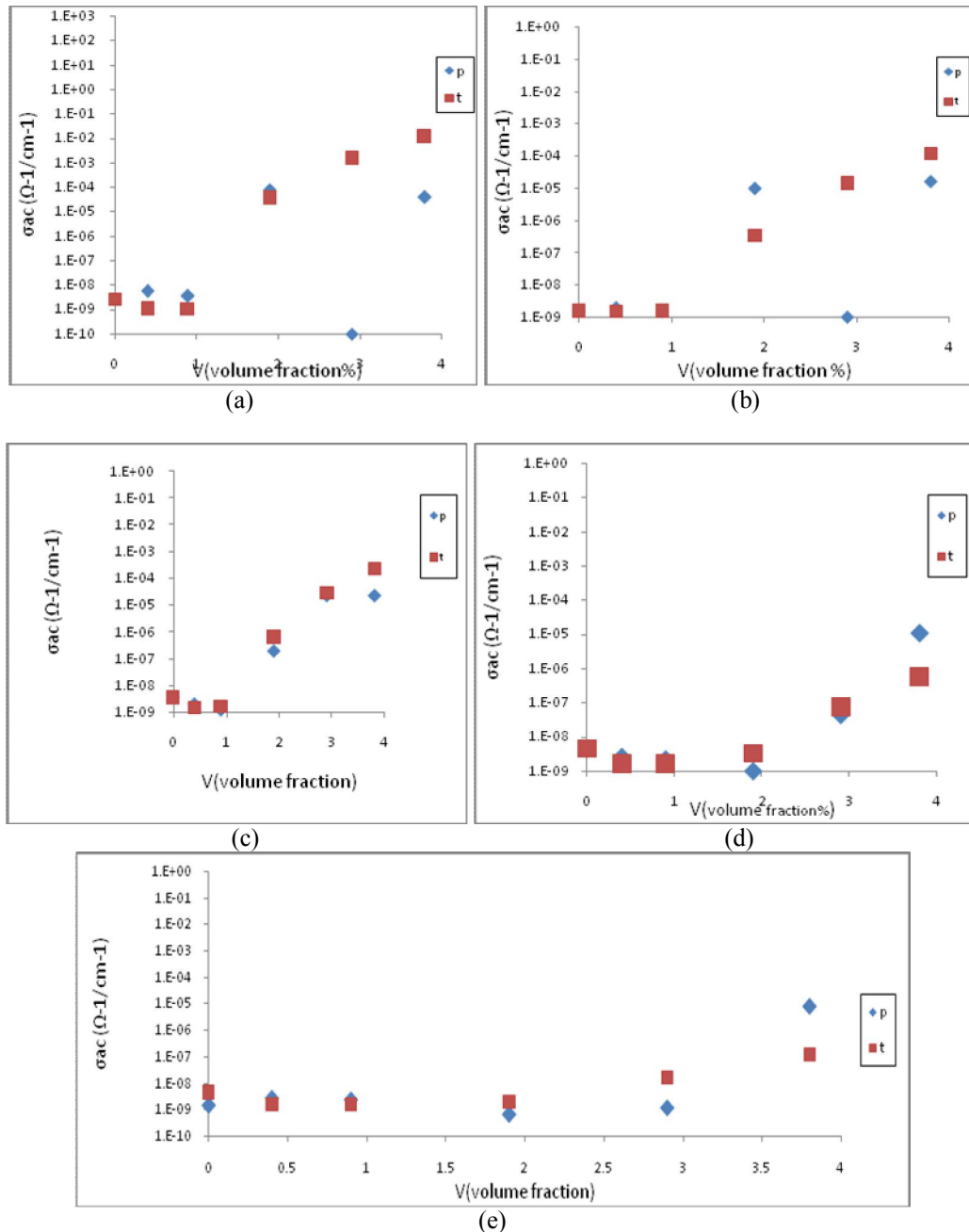
Figure(5 a-e): The theoretically calculated conductivities using Sohi et al model are very close to the experimentally determined conductivities for all laser irradiated composite systems (a=0J, b=50J, c=100J, d=150J, e= 200J).

2. Effect of Laser beam energy on d.c Electrical conductivity measurements[6]

Measurements of PVA- CNT composites as a function of CNT concentration was detected after samples exposure to laser beam energy (200 Joules) and comparing the results with that detected before laser irradiation. Each data point on the plot represents the average of measurements on 3-5 different samples.

The percolation threshold corresponds to the formation of a CNT network that allows electron transport by tunneling or electron hopping along CNT interconnects.

The individual percolation curves were calculated using the most common formulae for the conductivity and dielectric constant (V= filler concentration, V_c= percolation threshold, σ_m, σ_f=

matrix polymer and filler conductivities, ε_a= proportionality constant for dielectric constant).

For V <V_c

$$\sigma_{dc} = \frac{\sigma_m}{(V_c - V)^s} \qquad \varepsilon_{dc} = \frac{\varepsilon_a}{(V_c - V)^c} \qquad (4)$$

For V >V_c

$$\sigma_{dc} = \sigma_f (V - V_c)^t \qquad \varepsilon_{dc} = \frac{\varepsilon_a}{(V - V_c)} \qquad (5)$$

At V = V_c (Using equations (4), (5)

$$\sigma_{dc} = \sigma_f \left(\frac{\sigma_m}{\sigma_f}\right)^{\frac{t}{(s+t)}} = \sigma_m \left(\frac{\sigma_f}{\sigma_m}\right)^{\frac{s}{(s+t)}} \qquad (6)$$

The loss tangent assumes its" universal value" given by $tan\left[\left(\frac{\pi}{2}\right)\left(\frac{s}{s+t}\right)\right]$[7,8]. It is used to calculate the dielectric constant at the percolation threshold according to:

$$\varepsilon_{dc} = \frac{4\pi\sigma_{dc}}{\omega}\left(tan\left(\frac{\pi}{2}\frac{s}{s+t}\right)\right) \qquad (7)$$
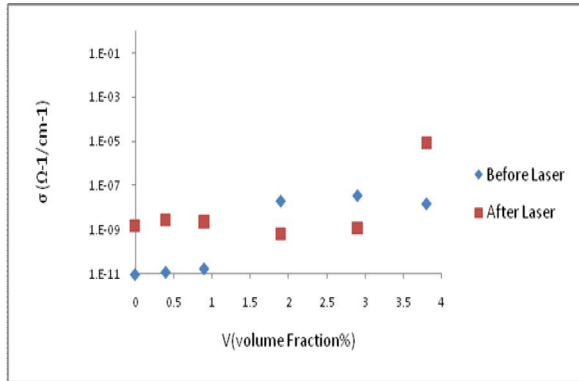

Figure (6): The matrix polymer and filler conductivities before and after laser irradiation

Where σ_{dc} is given by equation (3.6). Here, the critical exponents (before and after laser beam irradiation) are s= 0.937 and t= 1.407 (before) and s= 1.5 and t = 1.367 (after) respectively.

For the curve in Figure (6) the matrix polymer conductivity and filler conductivity are σ_m=$10^{-15}\Omega^{-1}cm^{-1}$ (before laser irradiation)

$\sigma_m = 10^{-13} \Omega^{-1}cm^{-1}$ after laser irradiation and $\sigma_f = 10^4 \Omega^{-1}cm^{-1}$with these values since equation (6) is valid at the percolation threshold only, it can be used to determine the percolation threshold using experimental data simply by finding the filler concentration at which equation (6) is fulfilled.

It is clear that PVA sample loaded with 0.019 fulfilled this condition before and sample loaded with 0.029 after laser irradiation fulfilled with conditions.

3. **Laser induced modification in the Microwave Shielding properties of PVA/CNT composites**[9]

The use of lasers in polymer science has become a vast field of interest[10]. Lasers are used as analytical tools and many applications like material processing and information storage.

Electromagnetic interference (EMI) shielding refers to the reflection and/ or absorption of electromagnetic radiation by a material, which thereby acts as a shield against the penetration of the radiation through the shield. As electromagnetic radiation, particularly that at high frequencies tend to interfere with electronics (e.g. computers), EMI shielding of both electronics and radiation source is needed and is increasingly required by governments around the world. The importance of EMI shielding relates to the high demand of today's society on the reliability of electronics and the rapid growth of radio frequency and microwave radiation sources [11-13].

The primary mechanism of EMI shielding is usually reflection. For reflection of the radiation by the shield, the shield must have mobile charge carriers (electrons or holes) which interact with the EM fields in the radiation. As a result, the shield tends to be electrically conducting, although a high conductivity is not required.

For example, a volume resistivity of the order of 1Ωcm is typically sufficient. However, electrical conductivity is not the scientific criterion for shielding, as conduction requires connectivity in the conduction path (percolation in case of a composite material containing a conductive filler), whereas shielding does not.

Although shielding does not require connectivity, it is enhanced by connectivity.

A secondary mechanism of EMI shielding is usually absorption. For significant absorption of the radiation by the shield should have electric and/or magnetic dipoles which interact with the electromagnetic fields in the radiation.

The reflection loss decreases with increasing frequency, whereas the absorption loss increases with frequency.

Other than reflection and absorption a mechanism of shielding is multiple reflection, which refer to the reflection at various surfaces or interfaces in the shield.

The losses, whether due to reflection,absorption or multiple reflection, are commonly expressed in dB. The sum of all the losses is shielding effectiveness (in dB). The absorption loss is proportional to the thickness of the shield.

Electromagnetic radiation at high frequencies penetrates only the near surface region of an electrical conductor. This is known as the skin effect. The electric field of a plane wave penetrating a conductor drops exponentially with increasing depth into the conductor. The depth at which the field drops to 1/e of the incident value is called skin depth(δ) which is given by:

$$\delta_D = \frac{1}{\sqrt{\pi f \mu \sigma}} \qquad (8)$$

Where f = frequency, μ = magnetic permeability = $\mu_0 \mu_r$

μ_r = relative magnetic permeability, $\mu_0 = 4\pi * 10^{-7} Hm^{-1}$, and

σ = electrical conductivity in $\Omega^{-1} cm^{-1}$.

Polymer-matrix composites containing conductive fillers are attractive for shielding[14-16] due to their process-ability (e.g. mold-ability), which helps to reduce or eliminate the seams in the housing that is the shield. The seams in are commonly encountered in the case of metal sheets as the shield and they tend to cause leakage of the radiation and diminish the effectiveness of the shield. In addition, polymer matrix composites are attractive in their low density. The polymer matrix is commonly electrically insulating and does not contribute to shielding, though the polymer matrix can affect the connectivity of the conductive filler and connectivity enhances the shielding effectiveness. In addition, the polymer matrix affects the process ability.

For a general EMI shielding material in the form of a composite material, a filler that is effective at a low concentration is also desirable, although it is not as critical as for EMI gasket.

This is because the strength and ductilibility of a composite tend to decrease with increasing filler content when the filler-matrix bonding is poor. Poor bonding is quite common for thermoplastic polymer matrices. Furthermore, a low filler content is desirable due to greater process ability, which decreases with increasing viscosity. In addition, a low filler content is desirable due to the cost saving and weight saving.

In order for a conductive filler to be highly effective, it preferably should have a small unit size (relative to the skin depth), a high conductivity (for shielding by reflection) and a high aspect ratio (for connectivity). Carbon nanotubes are attractive than particles due to their high aspect ratio.

Referring to equation (8) and the measured dc conductivity for all samples and the measured data for CNT, μ_r = 0.144, σ = 1*10^4 $\Omega^{-1} m^{-1}$. Using the mixing law equation for calculating the relative permeability of the polymer composite by knowing μ_r of CNT filler and μ_r of the PVA (=10)[17] and the mixing volume ratio V which has the form of :

$$\mu_m = \mu_f V - \mu_p (1 - V) \qquad (9)$$

One can deduce that the skin depth (δ) as a function of both the volume fraction of the filler and the irradiated accumulated dose (200J) of the laser beam as shown in Figure (7).
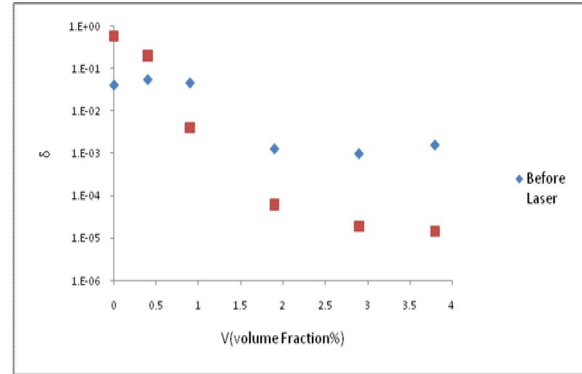

Figure (7): The skin depth(δ) as a function of both the volume fraction of the filler and the irradiated accumulated dose (200J) of the laser beam

From Figure (7) one can observe that the skin depth decreases with the increasing contents of CNT by approximately 400 times its initial value by loading the matrix by (0.038) of CNT. Meanwhile, this ratio of decreasing is rise to be 4 orders of magnitude after exposing the samples to accumulated laser beam of 200J.

PVA sample loaded with (0.038) CNT and irradiated with 200J of laser beam as obviously clear from Figure (8) which represent the total shielding effectiveness (S_{ET}) as a function of the measured frequency range.
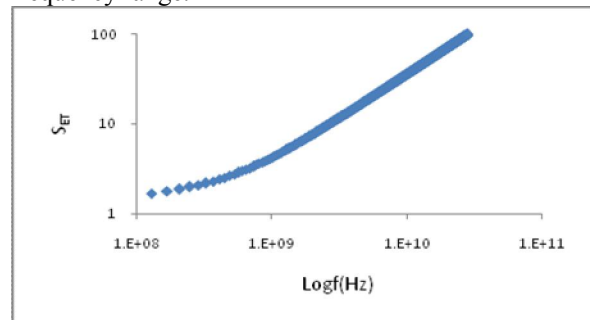

Figure (8): The total shielding effectiveness (S_{ET}) as a function of the measured frequency range of PVA sample loaded with (0.038) CNT and irradiated with 200J of laser beam

As expected from the above figure the maximum value (129.5 dB) of the SE_T is obtained at (36.5GHz) for the composites with V= (0.038) after exposed to (200J) laser beam.

4. Conclusion:

The percolation threshold was appreciably changes from 0.019 to 0.029 by laser beam energies up to 200 Joule. By using Sohi et al[4] model, one could interpret the change in the percolation threshold owing to the change of the geometric factor that

defines the geometry arrangement of conductive chains and their overlap in the PVA matrix.

The skin depth decreases with the increasing of CNT (to 0.04 V. fraction) by approximately 400 times its initial value and increases by four-order of magnitude upon irradiated the samples by 200 Joule laser-beam.

The maximum value of SE_T (129.5dB) is obtained (at 35 GHz) for the irradiated composite loaded with 0.038.

Correspondence Auther:
Name: Ashraf S. AbdelHaleem.
Work address: Armed forces, Egypt
e-mail address: ashraf_20091@hotmail.com

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