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Investigations of the electrical properties of LASER irradiated single walled carbon nanotubes loaded polymethyl-metha acrylate

Gamal. M. nasr
Physics Department, Faculty of Science,
Cairo University
Egypt.
rrrrrgamal@yahoo.com

Mohamed A. Ali
Physics Department, Faculty of Science,
Cairo University
Egypt.
mohamedali@sci.cu.edu.eg

M. Abu-Abdeen
Physics Department, Faculty of Science,
Cairo University
Egypt.
mmaabdeen@sci.cu.edu.eg

Magdy Omar
Physics Department, Faculty of Science,
Cairo University
Egypt.

***Abstract*—Single walled carbon nanotubes (SWCNTs) have wide range of applications. Commercial**

SWCNTs have impurities, disorder and entangled structure, which limit its applications. In this respect, laser treatment with different doses was applied to enhance its structure. In this work polymethyl methacrylate as a polymer host was loaded with different concentrations of as received and laser treated SWCNTs at different doses to get two group samples, one loaded with as received SWCNTs and the other loaded with laser treated SWCNTs at different dose. Alternating current electrical conductivity was found to increase as SWCNTs loading increased in a percolation behavior with a percolation threshold value of 0.46 weight percent. Laser treatment of SWCNTs for a concentration of 0.5 weight percent (close to the percolation threshold) increased the ac electrical conductivity. On the other hand, 20 mJ laser dose rapidly decreased the conductivity of samples containing 1.0 weight percent SWCNTs, while further doses (50 and 100 mJ) increased the conductivity to a value close to the non-treated sample. The addition of untreated SWCNTs as well as the laser doses treatment of samples containing 0.5 weight percent result as a formation of semi-circles in Cole-Cole plots with the radii decreased as the content of CNTs or laser doses increased.

Keywords—SWCNT; PMMA; Laser treatment; casting

I- INTRODUCTION

From the academic and industrial points of view, single walled carbon nanotubes (SWCNTs) have been the research focus and considered the most popular nanomaterials after C60 because of their unique and remarkable electrical, thermal optical and mechanical properties [1][2][3][4][5]. Carbon nanotubes (CNTs) tend to agglomerate in bundles and their dispersion in many polymers is limited and this is reflected as limitations in polymers loaded CNTs nanocomposites applications. The development of the electrical and mechanical properties of polymers loaded with CNTs depends strongly on the degree of dispersion of CNTs through the polymer matrix as well as the interaction between them and polymer chains. The challenge is the breaking of these CNTs aggregates to allow fine dispersion in matrices. The dispersion of CNTs through polymers was improved by several approaches. Ultra-sonication and high shear mixing are the mechanical or physical approaches for dispersing CNTs. Surfactant addition, melt blending and chemical modification through surface functionalization to prevent CNTs agglomerations represent another approach. That are different from those of the original nanotube[4], [6]. A change of hybridization from sp2 to sp3 is associated during direct covalent sidewalls functionalization with a simultaneous loss of the -conjugation system on the CNTs walls [7], [8].

Various applications needed specific surface properties in polymeric materials. The surface properties of polymer could be treated by laser beam to obtain polymers with desired surface properties in various substance[9]. The laser treatment is an convenient way for treating polymer surfaces[10]–[13]. A more general approach to nanoparticles dispersed in polymers is nanoparticle treatment using pulsed laser ablation. This versatile technique has attracted growing interest for a number of materials and liquids during the last two decades [14]–[17].

In the present work two group samples are prepared. The first group is prepared via incorporating as received SWCNTs with different weight ratios in

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PMMA polymer matrix as host material using casting technique. On the other hand, SWCNTs are previously treated with different doses of laser and then incorporated in PMMA matrix using casting technique which is the second group samples. The alternating current electrical properties; namely, ac electrical conductivity and electrical impedance of both groups are studied.

II- EXPERIMENTAL

A. *Materials*

The polymerization of Poly Methyl Methacrylate (PMMA) matrix was performed with Benzoyl peroxide supplied by BDH (England) as an initiator. Methyl methacrylate is an organic compound with the formula CH2=C(CH3)COOCH3. It is colorless liquid, the methyl ester of methacrylic acid (MAA) is a monomer produced on a large scale for the production of PMMA contents. Methyl Methacrylate solvent has (Mw = 100.12 g/mol) and density equal to 1.18 gm/cm3 with purity 99% was supplied by (RESERCH-LABFINE CHEM INDUSTRIES) Company. The initiator uses for prepared PMMA is Benzoyl peroxide. The purified monomer MMA (12.94) mL, was taken in a polymerization tube and 0.0485 g of benzoyl peroxide which act as catalyst was added to accelerate the polymerization in the polymerization reaction. The polymerization tube was then taken in water bath at 333-343 K in an electric oven for three days. A hard viscous polymer was obtained after three days of heat treatment[18].

Single walled carbon nanotubes SWCNTs, (Aldrich 704113) with outer diameter of 0.7–1.3 nm and average length of 800 nm was purchased.

B. *Samples preparations*

Initially, a certain weight of previously prepared PMMA was dissolved in chloroform at room temperature with a magnetic stirrer for 2 h. The desired amounts of as received SWCNTs (0.0, 0.5, 1.0, 2.5 and 5.0 wt%) were dissolved chloroform and ultra-sonicated for 30 min followed by magnetic stirring for further 24 h to get SWCNTs solutions. Other weight ratios of previously laser treated SWCNTs with different doses (20, 50 and 100 mJ) solutions were also prepared to get laser treated SWCNTs solution. The sonicated two groups of SWCNTs solutions were added to previously dissolved PMMA solutions to obtain polymer-SWCNTs solutions (one for as received SWCNTs and the other for laser treated SWCNTs). Both solutions were sonicated again for 30min, stirred for 24 h, and then cast in horizontal petri dishes and dried under ambient conditions to get two group samples. The first group represents PMMA polymer loaded with different concentrations of as received SWCNTs. The second group represents PMMA polymer loaded with different concentrations of previously laser treated SWCNTs at room temperature.

C. *Characterization*

Samples used for electrical and dielectric measurements were in the form of discs with dimeter of 10 mm and thickness of 0.1 mm. The electrical and dielectric quantities in the frequency range 10^{-1}–10^{7} Hz were achieved for all investigated samples utilizing Novocontrol high-resolution alpha dielectric analyzer. This technique is supported by Quatro temperature controllers, using pure nitrogen as a heating agent and assuring temperature stability better than 0.2 K. The measurements were conducted using gold-plated brass electrodes of diameter 10 mm for upper electrode and 20 mm for the lower one in parallel plate capacitor configuration. All measurements were carried out at room temperature. The complex dielectrics function $\varepsilon^*(\omega,T) = \varepsilon^{/}(\omega,T) - \varepsilon^{//}(\omega,T)$ where $\varepsilon^{/}$ is the permittivity and $\varepsilon^{//}$ is the dielectric loss was obtained. It is equivalent with the complex conductivity function $\sigma^*(\omega,T) = \sigma^{/}(\omega,T) + \sigma^{//}(\omega,T)$ since, $\sigma^*(\omega,T) = i\omega\varepsilon_o\varepsilon^*(\omega,T)$, implying that $\sigma^{/} = \varepsilon_o\omega\varepsilon^{//}$ and $\sigma^{//} = \varepsilon_o\omega\varepsilon^{/}$ (ε_o being the vacuum permittivity). The complex impedance is given by $Z^* = Z' + iZ'' = \frac{1}{i\omega_o\epsilon^*}$.

III. RESULTS AND DISCUSSION

A. *.Electrical conductivity of as received and laser treated SWCNTs loaded PMMA*

The ac electrical conductivity of the prepared samples are studied, especially the electrical percolation threshold. Figure 1 represents the dependence of the ac electrical conductivity on frequency, $\sigma(f)$, for the pure PMMA and the nanocomposites loaded with various contents of non-laser irradiated SWCNT at room temperature (300 K).

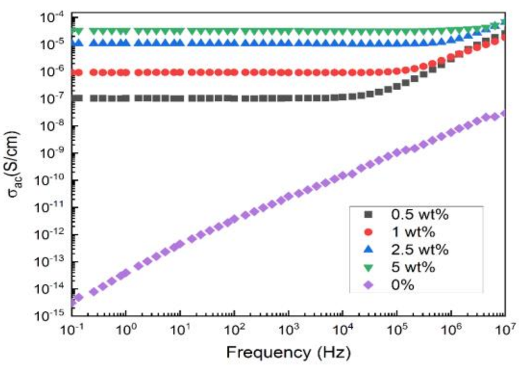

Figure (1): Dependence of the ac. Conductivity of pristine PMMA and its composites filled with non-irradiated SWCNT.

The ac conductivity for pure PMMA increases linearly with frequency, showing a typical behavior of insulating materials. On the other hand, samples with loading ≥ 0.5 wt% SWCNT exhibit a critical frequency fc (depends on SWCNT loading) separates two regions, frequency independent region of its □ac and dependent one. The frequency independent region (plateau one) is corresponding to dc conductivity σ_{dc}, where the electrical conductivity σ is independent of frequency below this critical frequency. The values of this critical frequency are 0.032, 0.31, 1.0 and 4.4 MHz for 0.5, 1.0, 2.5 and 5 wt% of SWCNTs; respectively. This independence behavior is extended in the whole frequency range as the SWCNT content increases and it is a characteristic behavior of conducting materials[9].

Figure 2 represents the ac conductivity dependence on the SWCNT Vol% concentration (at frequency 100Hz). It is clearly observed a transition from the insulating to the conductive phase at the so-called percolation threshold (vc), which is observed between 0.22 vol% and 0.44 vol%. The ac conductivity shows a nearly saturation behavior with SWCNT contents higher than 1.76 vol%. The increment in ac conductivity from 0.0 to 0.22 vol% SWCNT is marginal but thereafter an abrupt increase in conductivity for change in filler concentration from 0.22 vol% to 2.2 vol% is noticed. Hence, 0.41 vol% of SWCNT loading for PMMA matrix is considered as percolation threshold limit. At this critical loading, there is a formation of continuous conductive network of SWCNTs inside the polymer matrix, which reflects the drastic increase in the ac conductivity.

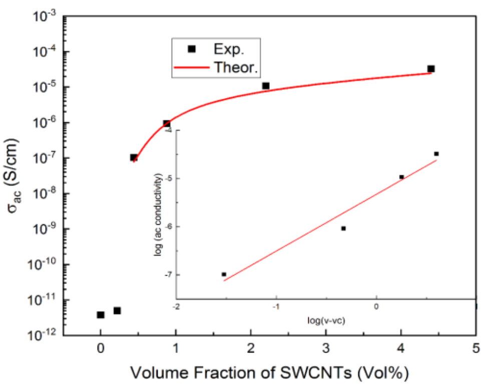

Fig. 2: Dependence of ac electrical conductivity of PMMA loaded with different volume fractions of SWCNTS at room temperature and 100Hz.

The expected value of the electrical percolation concentration of the ac. conductivity can be predicted using the scaling law equation:

$$\sigma_{ac} \approx (v - v_c)^s \qquad (1)$$

where v is the volume fraction of SWCNT, s is the critical exponent related to the dimensionality of the tested system and σ_{ac} is the ac conductivity. The plot of log σac versus log (v-vc) according to the scaling law equation, is shown as an inset of Figure 2. The solid line in Figure 2 represents the best fit for $v_c = 0.41$ vol. % (corresponding to 0. 46 wt. %), and $s = 1.17714 \pm 0.1646$. From the excluded volume theory[9], one can calculate theoretically the percolated volume v_c of SWCNT filler.

Figure 3 (a and b) illustrates the frequency dependence of ac conductivity, σ_{ac} for 0.5 and 1.0 wt% different laser doses treated SWCNTs loaded PMMA samples at room temperature. For sample containing 0.5 wt% CNTs, laser doses (20 and 50 mJ) increase the electrical conductivity from $1x10^{-7}$ to $2.5x10^{-6}$ S/cm at relatively low frequencies. This may be due to the formation of a new orientational configuration of polymer chains with CNTs. On the other hand, for 1.0 wt% samples, 20 mJ laser dose suddenly decreases the electrical conductivity from $1x10^{-7}$ to $4x10^{-9}$ S/cm due to cession of polymer chains. Further higher laser doses of present samples increase the conductivity again close to the value of non-treated sample which reflects the redistribution of CNTs inside the polymer matrix. For both samples there is a critical frequency which separate two regions (as shown in Figures 3 (a and b)), depends largely on the applied laser pulse. The independent region increases with frequency up to 100KHz with laser treatment pulse ($\cong 100$ mJ), so, the laser treatment increases the characteristic behavior of the samples as conducting materials.

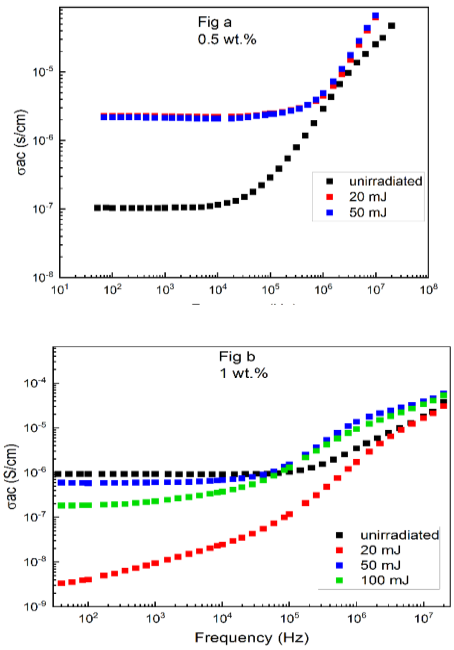

Figure 3: Frequency dependence of ac conductivity, σ_{ac} for laser treated SWCNTs/PMMA samples at room temperature.

B. *Impedance spectrum of as received and laser treated SWCNTs loaded PMMA*

Figures 4a and 4b represent the frequency dependence of real, Z/, and imaginary Z// parts of electrical impedance for PMMA loaded with different concentrations of untreated SWCNTs at room temperature. The main relaxation, which originates from orientation of dipoles is detected as maximum in $Z^{//}$ at frequency ω_{max} (as shown in the Figure (3.4) for all loaded samples except the neat one). With increasing CNTs loading in PMMA, the orientation of dipoles becomes more complicated, therefore ω_{max} slightly increases. The relaxation peak at frequency ω_{max} characterized by one relaxation time constant, $\tau(= \omega_{max}/2\pi)^{-1}$, where this relaxation is called Debye relaxation. Close looking to Figure (3.4), one could divide the spectrum into two regions according to the ω values. First region at $\omega \leq \omega_{max}$ (low frequency region) and the second one at $\omega \geq \omega_{max}$ (high frequency region). ω_{max} is observed to slightly increase with SWCNT loading as listed in Table 1.

Only one relaxation peak is detected (cf. Figure 4a) for all samples indicating a Debye relaxation (no interaction between dipoles). Moreover, at low frequency region, the $Z^{/}$ value is constant for all samples and has lower value with CNT loading. One could observe also, from Figure 4b that, there is a frequency at which $Z^{//}$ is minimum called minimum frequency ω_m observed in the low frequency region for all loaded samples reflecting the effect of electrode polarization. Moreover, the peak heights are proportional to the bulk resistance, R_b, which can be explained using the equation: $z^{//} = R_b\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right)$ in $Z^{//}$ versus frequency plots and listed in Table 1. One can notice that the bulk resistance decreases appreciably by increasing SWCNTs loading in the PMMA polymer matrix.

Table 1: The volume fraction dependence of relaxation peak frequency, relaxation time and the bulk resistance for all loaded samples

SWCNTs contents vol%	f_{max} (Hz)	τ_{max} (s)	R_b (10^4 Ohm)
0.44	4.70E+05	2.13E-06	609
0.88	2.40E+05	4.17E-06	0.69
2.2	2.10E+05	4.76E-06	0.38
4.4	2.00E+05	5.00E-06	0.29

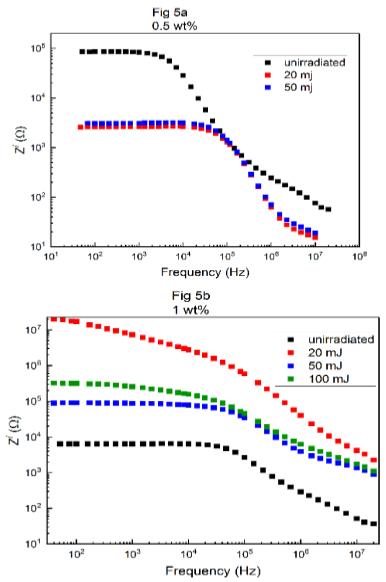

Figure 5 (a and b): The variation of the SWCNTs/PMMA samples imaginary part of impedance with frequency for different laser treatment doses.

Figures 5a and,5b show the variation of the SWCNT/PMMA (0.5 and 1.0 wt%) samples real part of impedance with frequency at different laser treatment doses. It can be observed that, the impedance Z/ of both samples at different laser treatment doses rapidly decreases by increasing frequency at values $\geq 10\text{KHz}$. At low frequencies, $Z^{/}$ decreases rapidly from 10^5 to $2\text{x}10^3$ Ω for 0.5 wt% SWCNTs/PMMA when laser treated which in a good agreement with the electrical conductivity represented in Figure 3a. Samples loaded with 1.0 wt% of laser treated CNTs with a dose of 20 mJ, on the other hand, $Z^{/}$ suffers an abrupt increase from $8\text{x}10^3$ to $2\text{x}10^7$ Ω. As the laser dose increased, $Z^{/}$ returns back and decreases to 10^5 Ω for 100 mJ laser dose which, also in a good agreement with the electrical conductivity shown in Figure 3b.

Figures 6a and 6b show the dependence of the imaginary part of impedance on frequency for laser treated 0.5 wt% and 1.0 wt% SWCNTs/PMMA at room temperature. From the Figure, one can notice that, the main relaxation, which originates from orientation of dipoles and defected as a maximum in $Z^{//}$ for untreated samples was vanished upon treatment. Moreover, for sample 1wt% at laser doses ≥ 20 mJ the $Z^{//}$ value decreases with increasing frequency as only detected behavior for all treated samples under different laser doses for PMMA samples loaded with 1 SWCNT wt%. Meanwhile, this behavior is detected after laser treatment with dose ≥ 100 mJ pulse for PMMA sample loaded with 0.5 SWCNT wt%. The value of ω_m increased with laser treatment dose for PMMA loaded with 1wt% of SWCNT. The peak height detected in Figure (5b) decreases with laser treatment dose.

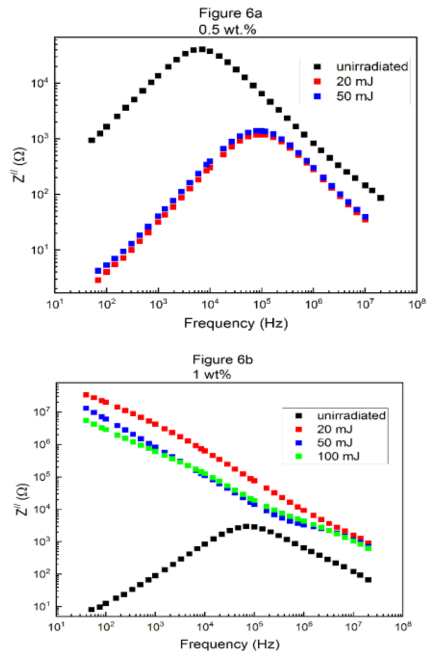

Figure 6 (a and b) : The variation of the SWCNTs/PMMA samples imaginary part of impedance with frequency for different laser treatment doses.

C. 3.3 Cole-Cole plot

Figures 7 and 8 show the complex impedance spectrum (Cole-Cole plots) of the untreated and laser treated composites obtained at room temperature over frequency range (0.1Hz-10MHz); respectively. One can observe the formation of the semicircular arcs whose pattern of evolution changes with CNT loading in PMMA matrix and laser treatment. The kind of electrical process occurring within the polymer matrix could be extracted from the extent of the intercept of semicircles on the real axis ($Z^{/}$-axis). The semicircular arcs are mainly attributed to a parallel combination of resistance and capacitance. With the increase of CNT loading, the radius of the semicircular arc generally decreases. In the present study, depressed semi-circles of non-Debye type of relaxation are noticed, so, instead of a single relaxation, a distribution of relaxation time is expected [10-11] . The characteristic peak of the semicircles occurred at a unique relaxation frequency called resonance frequency ($f_r = 1/2\pi RC = 1/2\pi\tau$) where τ is the relaxation time. The value of the bulk and grain boundary resistance is detected from the intercept of each semi-circle on real $Z^{/}$-axis and presented in Table 2 for untreated samples.

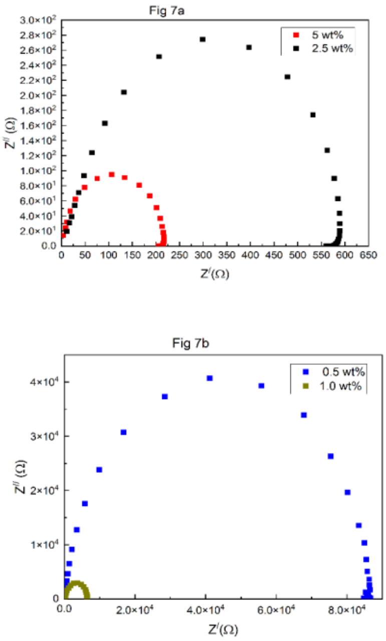

Figure 7: The Cole-Cole Plots of all untreated SWCNTs/PMMA composites at room temperature.

Table 2: The variation of both bulk and grain boundary resistances of all untreated loaded composites as a function of SWCNT volume fraction loading.

Volume fraction of SWCNT (vol.%)	Bulk resistance (Ohm)	Grain boundary resistance (Ohm)
0.44	85249.9	56.689
0.88	6392.47	36.7514
2.2	560.545	11.1678
4.4	204.686	3.62885

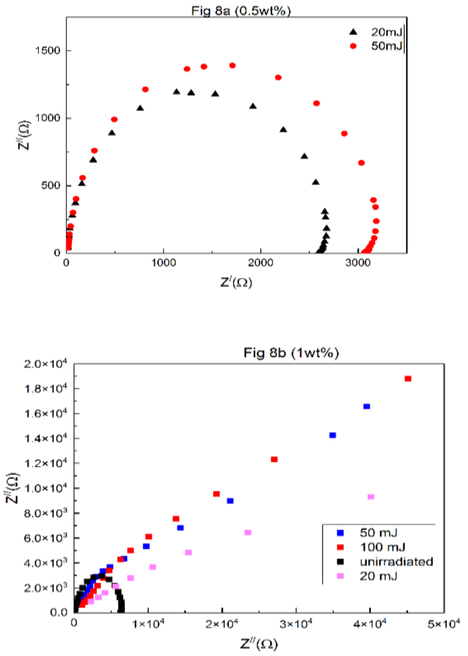

Figure 8: Cole-Cole Plots for samples loaded with 0.5wt% and 1.0 wt% of CNTs and treated with different doses of laser at room temperature.

CONCLUSIONS

From this work one can have many conclusions. The addition of single walled carbon nanotubes to polymethyl methacrylate increases the electrical conductivity according to the percolation behavior with a threshold percolation concentration equal 0.46 wt%. The addition of SWCNTs to PMMA polymer matrix, also, decreases the electrical impedance and leads the formation of semicircular Cole-Cole plots with radii decreased with increasing CNTs content. Laser treatment of samples containing SWCNTs with concentrations in the range of percolation region (0.5 and 1.0 wt%) has a pronounced effect on the electrical properties. The electrical conductivity of samples containing 0.5 wt% SWCNTs (close to the percolation threshold value) is increased with increasing the doses of laser. Concentration of SWCNTs of 1.0 wt% (slightly far from percolation threshold) is less sensitive to laser doses than 0.5 wt%.

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