Electrical Properties of PMMA / Dye Composite Irradiated With Laser

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Abstract: The use of polymer alloys blends and composites have grown constantly at 9% in the last 10 years and it is four times the growth rate of total plastic industry. In this study, we report the polymerization process of undoped and doped Polymethyl methacrylate (PMMA) with different dye concentrations .The dielectric properties of PMMA (undoped and doped) polymerized by laser beam irradiation have been compared with those polymerized with laser beam irradiation effects in order to establish the superiority of the laser beam irradiation process over the conventional polymerization. Compared to pure polymer, the dielectric constant of the dye- polymer composites is greater for all fill concentrations because the system becomes more heterogeneous than the pure polymer as more dye is added to it. The increase in ε′ with increase in dye is attributed to the formation of clusters, which lead to greater average polarization and thus a greater contribution to dielectric constant. In case of modified PMMA with dye concentration less than and equal to the percolation threshold, one could observe a gradual increase in ε′ with laser energy up to 100 Joules followed by an abrupt increase till 150 Joules. An RC electric equivalent circuit model was successfully for our sample to declare the effect of both dye concentration and laser beam energies on the dielectric properties of the tested samples.

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1. Introduction

Copolymer and doped copolymer are being an increasingly important class of material for a variety of applications in the electronics, optical solar collectors and electric industries [1-3]. The correlation between the degree of doped filler dispersion and the optical as well as the electrical properties is very high, so, it is considered one of the current methods to determine the degree of dispersion of filler within the copolymer matrix.

The dielectric spectroscopy has proven to be a very useful tool for studying the structure and the dynamics of polymeric systems [4-6].This knowledge is very important for development of new materials for technological applications, with specific electrical properties [7].

The effect of high energy irradiation on polymeric materials has been intensively studied over the past 70 years .These studies parallel the growth of polymeric materials and the availability of electrically generated radiation sources [8].The effect of radiation on materials has importance in the areas of wire and cable insulation, heat ,shrinkable , articles , curing of elastomers , plastics , paints , and inks electron beam lithography, inedical sterilisation , polymer property control and over space applications [9,10]. In general, the effects of exposure of polymers to high energy irradiation will lead to some change in the properties of the polymer.

Irradiation process is known to imitate several processes which include, e.g. displacement, mixing, radiation enhanced diffusion, and radiation enhanced segregation[11]. Further the investigation on radiation –enhanced short range ordering and clustering precipitation and self –diffusion has also been reported [12].

Laser -beam irradiation could be used during the polymerization process of polymeric materials to enhance their properties.

Polymethyl methacrylate (PMMA) readily degrades via chain scission with ε′ (scission) factor 2.28 [13] in vacuo and 0.5 in air [9], i.e. the rate of degradation is lower in air than in vacuo .

In this paper, we report the laser- beam irradiation effects of different energy during the polymerization process of undoped and doped PMMA with different dye concentrations .The dielectric properties of PMMA (undoped and doped) polymerized by laser beam irradiation have been compared with those polymerized with laser beam irradiation effects in order to establish the superiority of the laser beam irradiation process over the conventional polymerization.

2. Experimental

From Aldrish methylmethacrylate and rhodamine dye were purchased to be used in this study .Pure grad. benzoyl peroxide (BP) supplied by BDH (England) was used as an initiator. Thick films of pure PMMA with different dyes concentrations were prepared by thermal polymerization method [14].

The polymerization was performed with (BP) as an initiator (1 wt %) and the mixture was poured into a glass mold. The mold was then immersed in water path at 80^0C for 4h then at 60^0C for 72h, followed by a final drying at 80^0C for 4h. After curing , the samples were removed and then cut as desired .The MMA monomer was doped with different concentrations of Rhodamine dye (0,0.003,0.005,0.01,0.02,0.03 and 0.04 wt%).

Laser beam irradiation

A Laser beam source model Big Sky Nd-Yag Laser located at the National Institute of Laser Science, Cairo University was used for irradiating the samples during polymerization process at different energies (0-200J at 50J step).

The samples of PMMA doped with 0.003,0.005 and0.01 wt% dye were chosen to test the effect of Laser-beam irradiation energy during polymerization process at different polymerization time (at 0, 24h, and 48h) on their dielectric properties.

All samples were cut into disc form of 0.1 cm thick and 1cm in diameter for characterization by measuring dielectric properties using precision LCR meter HP 4284 at frequency range 100Hz to 2MHz, all samples were coated by silver paste to ensure good contacts.

3. Results and Discussion

a- *Concentration dependency of dielectric constant*

The variation of dielectric constant as a function of dye concentration at constant frequency (1000 Hz) is shown in figure (1).

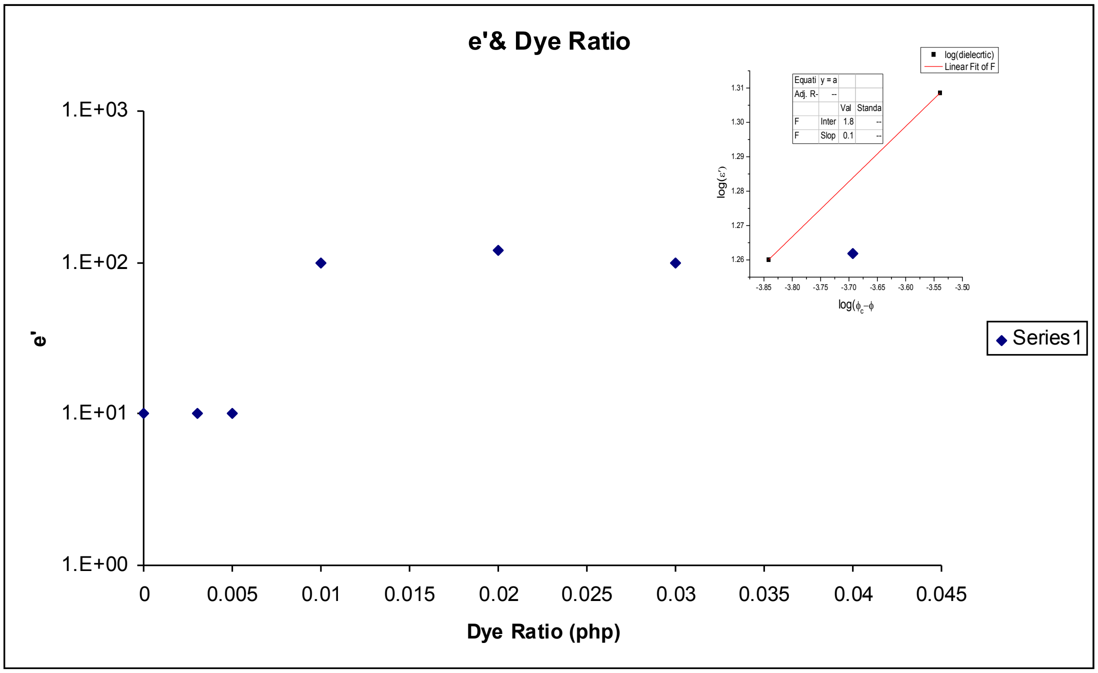


Figure (1): The variation of dielectric constant as a function of dye concentration at constant frequency (1000 Hz)

The following observations can be made from this figure:

(1) The dielectric constant increases slightly as the volume content of the dye in the polymer is increased.

(2) A dielectric singularity in the concentration range is detected at dye content (0.005%). The dielectric constant increases rapidly after this concentration (i.e. ε′ enhances greatly near Φ= 0.005wt %).

The ε′ of the composites in the low frequency region greatly enhances due to the Maxwell-Wagner polarization originating in the dye –polymer interfaces.This enhancement of ε′ in the neighborhood of the percolation threshold is also predicted by the power law [15-18] as follows :-

$\varepsilon'\alpha\ (\Phi_C-\Phi)^{-S}$ (1)

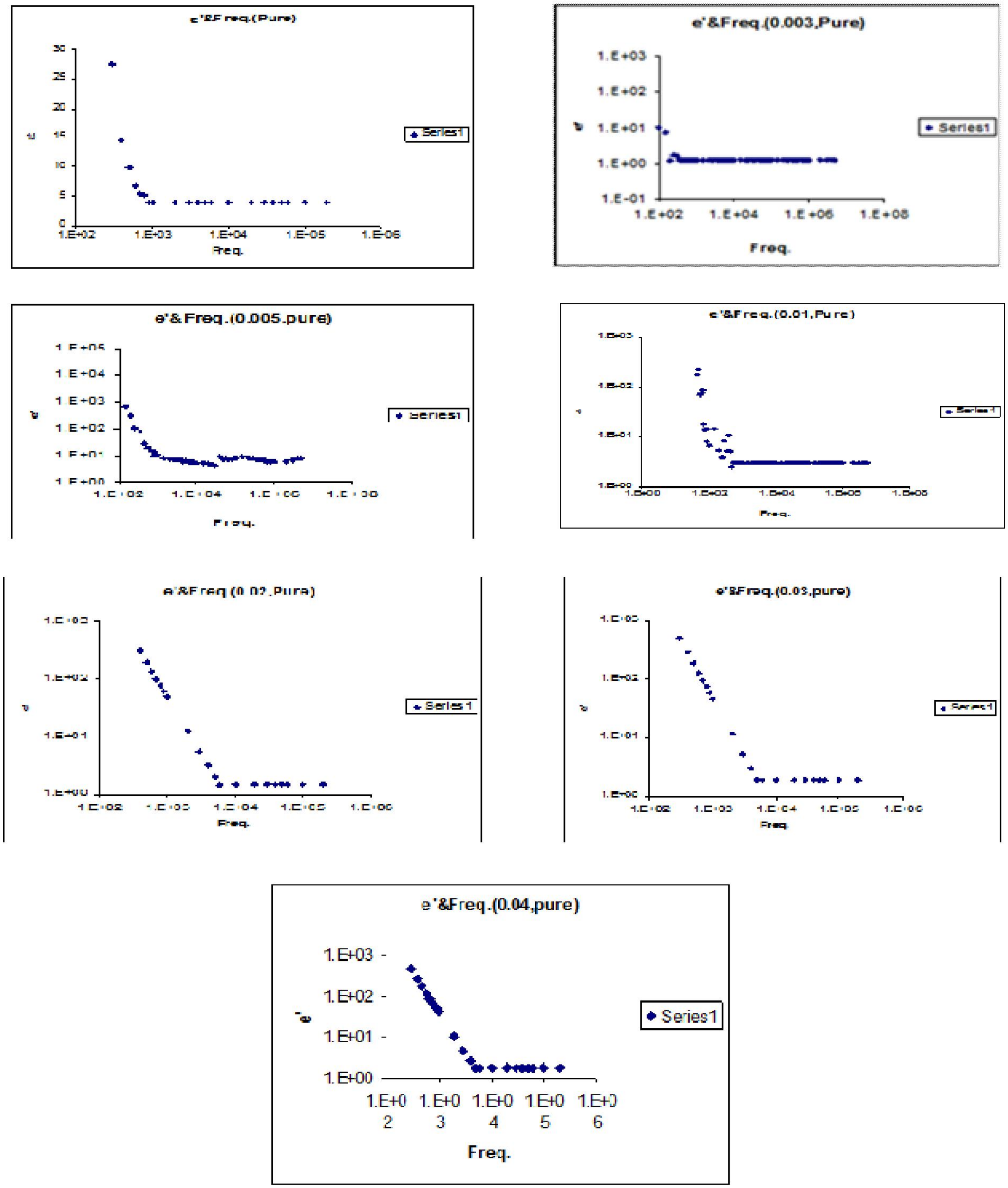
Where s is a critical exponent, Φ and Φ_c are the dye volume fraction and the critical volume fraction (percolation threshold) respectively. The log-log plots of equation (1) are shown in the inset of Figure (1)

The value of s was found to be (0.1) which is universal value given by percolation theory [15].

Compared to pure polymer, the dielectric constant of the dye- polymer composites is greater for all fill concentrations because the system becomes more heterogeneous than the pure polymer as more dye is added to it. The increase in ε′ with increase in dye is attributed to the formation of clusters, which lead to greater average polarization and thus a greater contribution to dielectric constant [19].

b- Frequency dependence

The dependence of ε' of PMMA –dye composites on frequency is shown in Figure (2 a-g).



G

Figure (2a-g): The dielectric constant ε′ decreases as frequency increases from 100 Hz to 2 MHz showing usual dielectric dispersion behavior.

When $\Phi < \Phi_C$ for example at $\Phi < 0.003$, the ε′ of the composites exhibits weaker frequency dependence, but when $\Phi > \Phi_C$, ε′ of the composites exhibits stronger frequency dependence.

It was observed from Figure (2.a-g) that the dielectric constant ε′ decreases as frequency increases from 100 Hz to 2 MHz showing usual dielectric dispersion behavior. In general the decrease in ε′ is rapid at lower frequencies and slower at higher frequencies. At low frequency, a relatively high value of ε′ of composites with $\Phi > \Phi_C$ was observed because at low frequencies, polarization follows the change of electric field, and the contribution to ε′ is maximum. At relatively high frequencies, the electric field changes too fast for the polarization effects to appear, Figure (2a-g).

The frequency dependence of the dielectric constant at $\Phi \sim \Phi_C$ as predicted by the percolation theory [6] is:

$\varepsilon'(f, \Phi_C) \; \alpha \; f^{-v}$ (2)

Where v is the critical exponent of the Log-Log plot of PMMA samples loaded with 0.005 % as an example of equation (2) is shown in Figure (3).

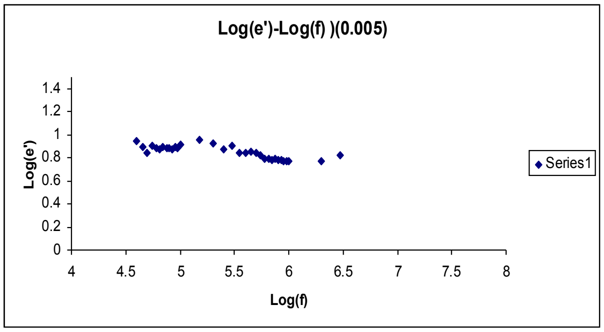
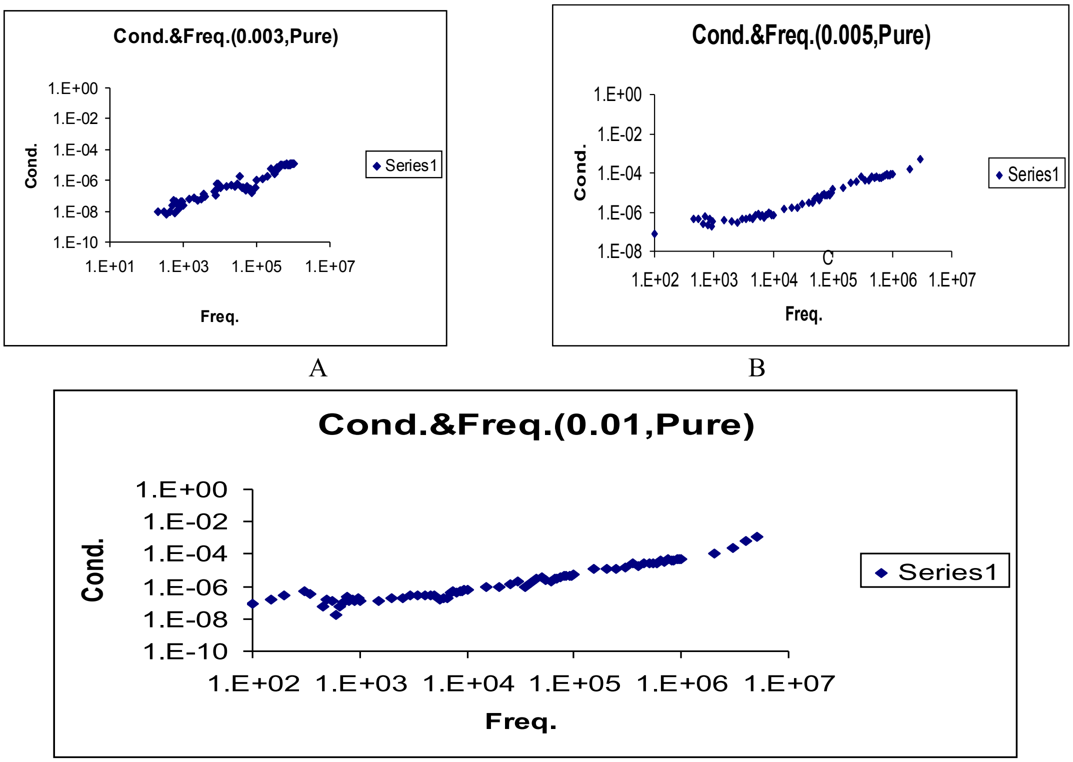


Figure (3): Log-Log plot of PMMA /dye percolated sample.

From the data, the value of v was found to be (0.089).

The dependence of the ac electrical conductivity of the PMMA/ dye composites on frequency is shown in Figures (4 a-c).



A B

C

Figure (4a-c): The dependence of the ac electrical conductivity of the PMMA/ dye composites on frequency

In most of the disordered solids; ac conductivity is directly proportional to the frequency. It is also well known that in large polaron hopping, the ac conductivity decreases with frequency whereas in small polaron hopping it increases with frequency [20,21]. In our case the plots of σ_{ac} with frequency are linear, indicating that the conduction is due to small polarons.

It has been shown that for ionic solids, the concept of small polaron is valid [22]**.** The dependence of σ_{ac} on frequency for $\Phi = \Phi_c$ according to the percolation theory is given as:-

$\sigma_{ac}(f, \Phi C) \alpha f^u$ (3)

Where u is the critical exponent of Log-Log plot of equation (3) is shown in Figure (5).

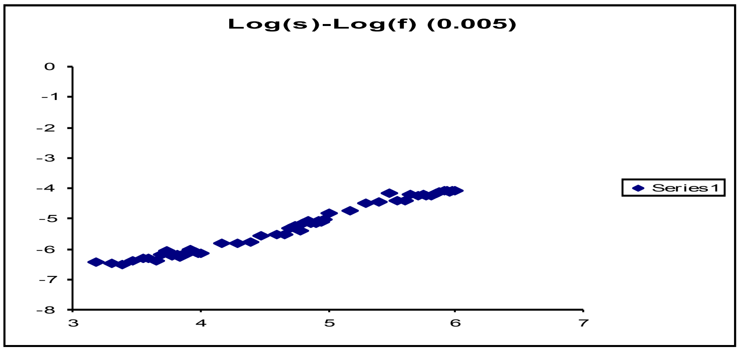


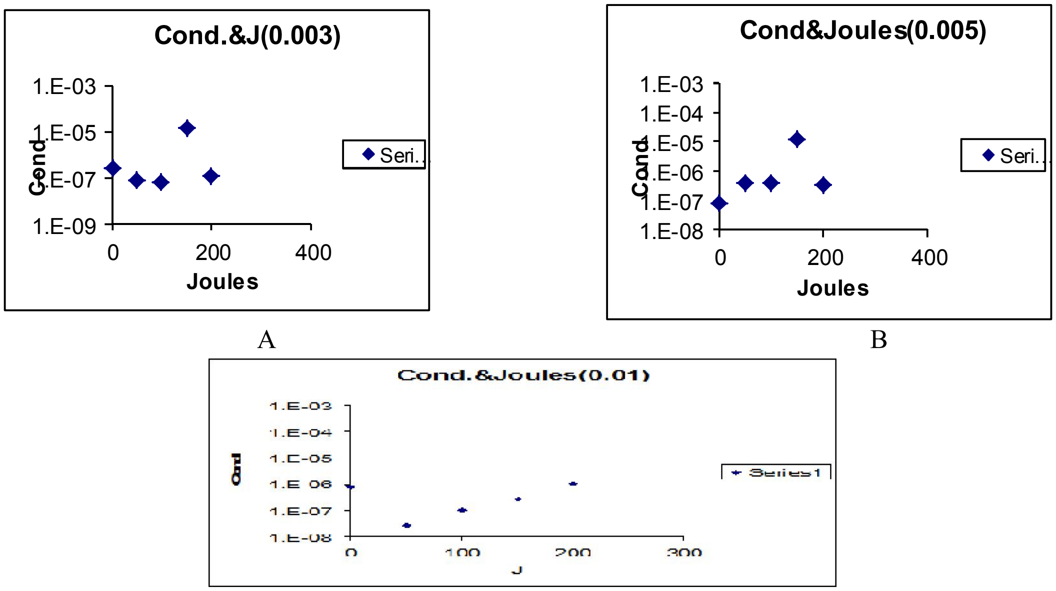
Figure (5): The dependence of σ_{ac} on frequency for Φ and Φ_C according to the percolation theory

From the data, the value of u was found to be (0.98) which is close to the normal value from the percolation theory [23].The critical exponent u and v are related as u+v =1. In our case u = 0.98 and v =0.089 i.e. u + v = 1.064. The above discussion nearly confirms the percolation phenomenon in PMMA/dye composites.

Effect of Laser beam irradiation energy during polymerization

The dielectric constant (ε′) is a measure of the influence of a particular dielectric on the capacitance. The dielectric constant tells how much smaller or bigger the space get. When a dielectric is put between two electric charges, it reduces the force acting between them, just as if they had been moved apart from each other [24].

Conductivity calculated at 100Hz, room temperature (300K) and at different laser beam irradiation energy (0, 50, 100, 150 and 200 Joule) during polymerization for PMMA loaded with 0.003,0.005 and 0.01 dye concentrations are present in Figure (6 a-c).

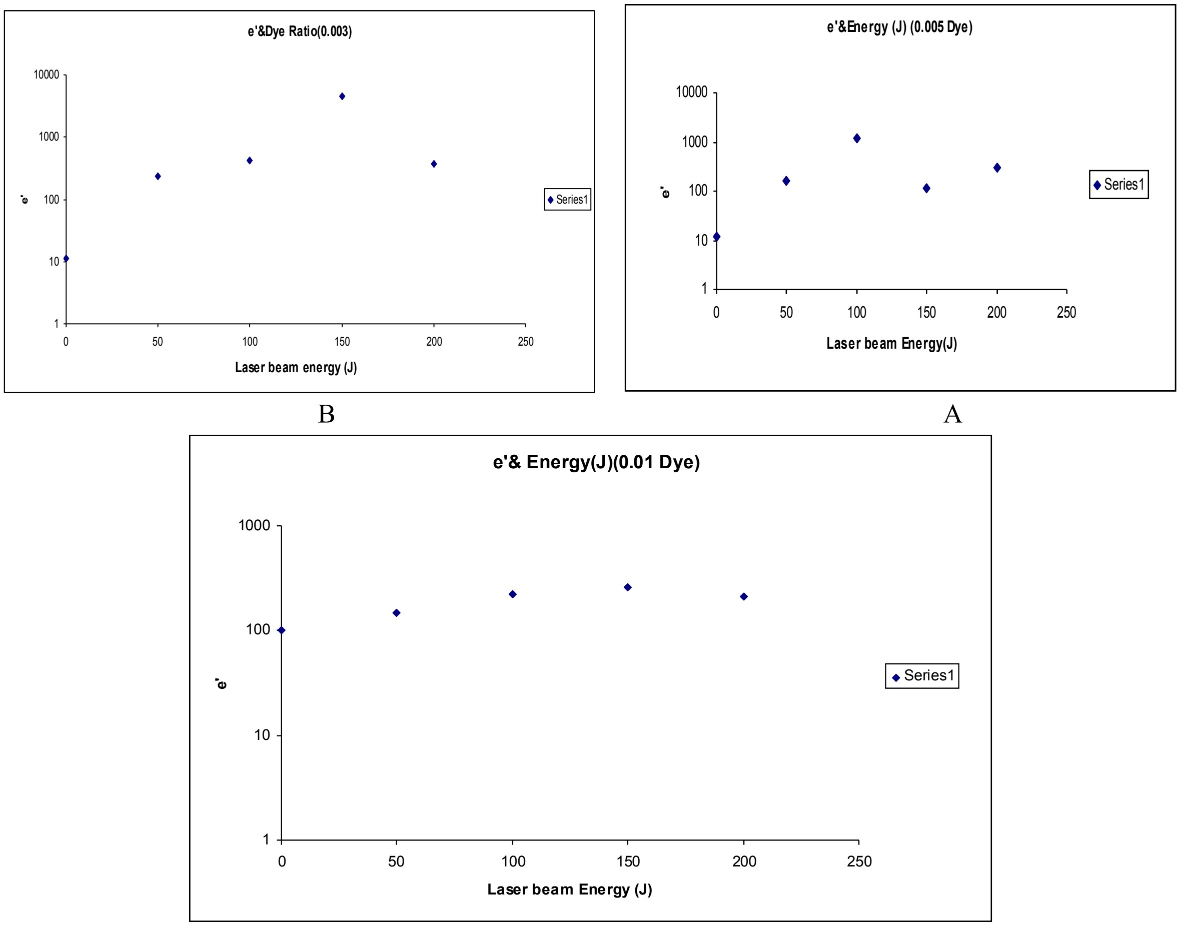


A B

C

Figure (6a-c): Conductivity calculated at 100Hz, room temperature (300K) and at different laser beam irradiation energy (0, 50, 100, 150 and 200 Joule) during polymerization for PMMA loaded with 0.003, 0.005 and 0.01 dye concentrations.

In case of modified PMMA with dye concentration less than and equal to the percolation threshold, one could observe a gradual increase in ε´ with laser energy up to 50 Joules followed by an abrupt increase till 150 Joules .This could be due to the increase of the quantity of accumulated charge (due to laser energy) which in turn increase the polarization effects. Polymethyl methacrylate (PMMA) modified by 0.01dye concentration show firstly an a gradual increase in its ε´ with laser beam (at 50 Joule) followed by a constant behavior of ε´ with increase laser energy which reflect the important role of dye concentration in the ε´ dependent of laser energy as illustrated in Figure (7a-c). Meanwhile the electrical conductivity of this sample increases linearly with laser energy greater than 50J.

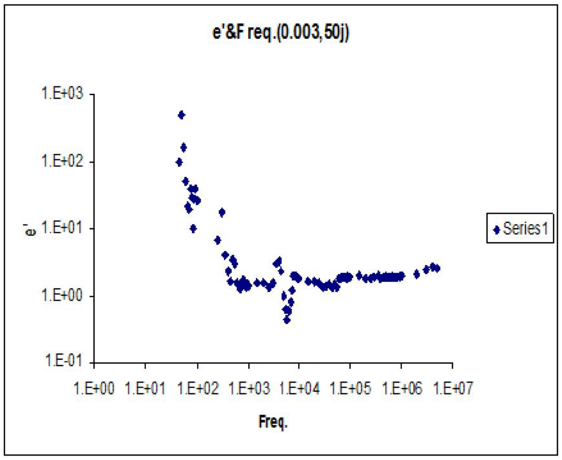


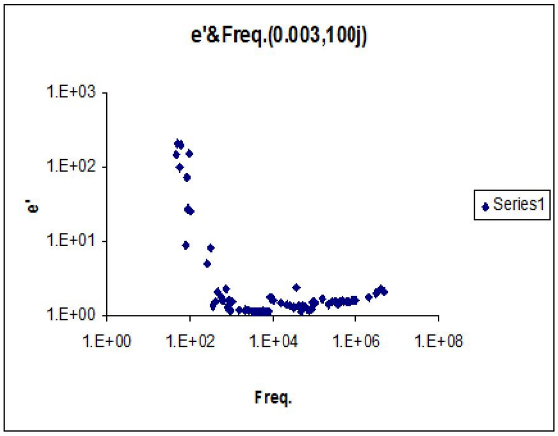
B A

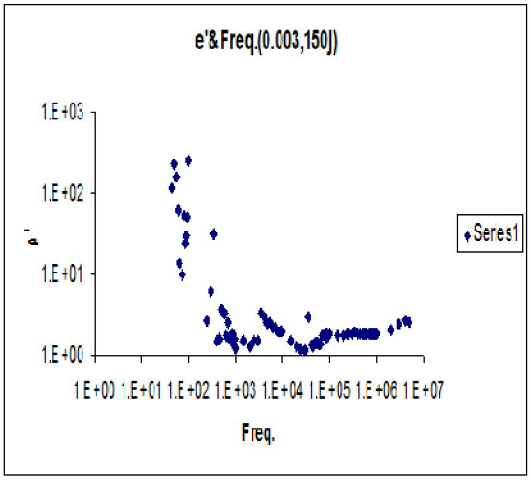
C

Figure (7a-c): The behavior of ε' of modified PMMA with dye concentration less than and equal to the percolation threshold (0.003, 0.005 and 0.01 %) with laser beam at (50, 100, 150 and 200 J).

Figures (8a-c) and (9a-c) illustrate the dielectric constant and conductivities of PMMA polymer and PMMA doped with dye concentration (0.003, 0.005 and 0.01wt %) after irradiated with different energy of laser beam during polymerization respectively.


e'&F req.(0.003,50j)
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
e'
1.E+00 1.E+01 1.E+02 1.E+03 1.E+04 1.E+05 1.E+06 1.E+07
Freq.
Series1


e'&Freq.(0.003,100j)
1.E+03
1.E+02
1.E+01
1.E+00
e'
1.E+00 1.E+02 1.E+04 1.E+06 1.E+08
Freq.
Series1


e'&Freq.(0.003,150j)
1.E+03
1.E+02
1.E+01
1.E+00
e'
1.E+00 1.E+01 1.E+02 1.E+03 1.E+04 1.E+05 1.E+06 1.E+07
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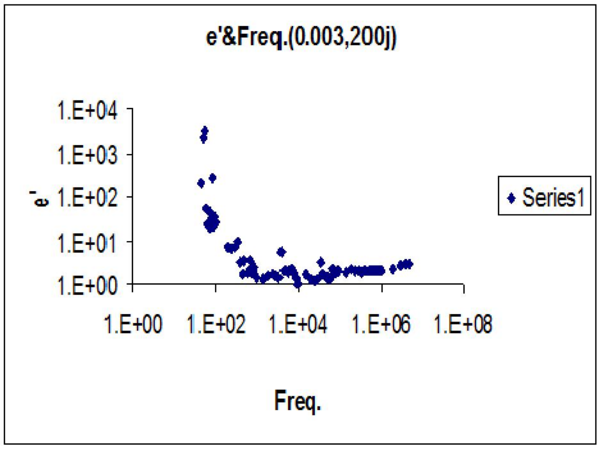
Seres1


e'&Freq.(0.003,200j)
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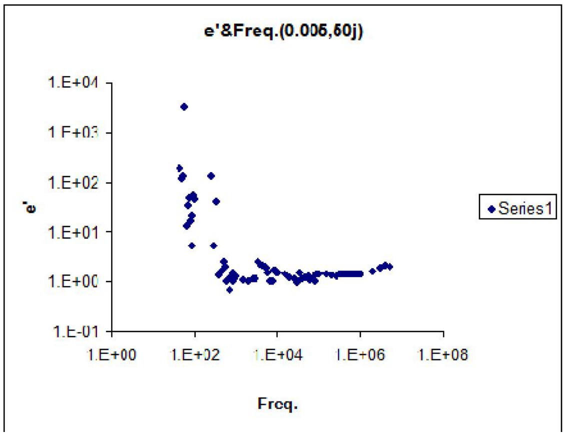
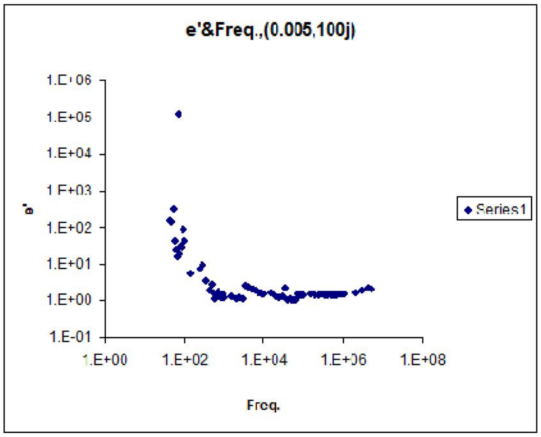
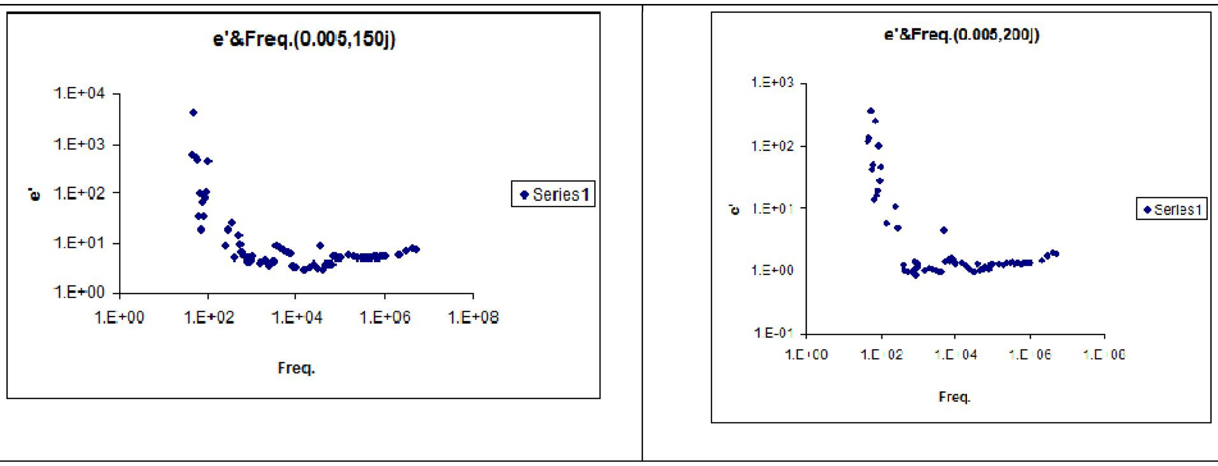
1.E+03
1.E+02
1.E+01
1.E+00
e'
1.E+00 1.E+02 1.E+04 1.E+06 1.E+08
Freq.
Series1

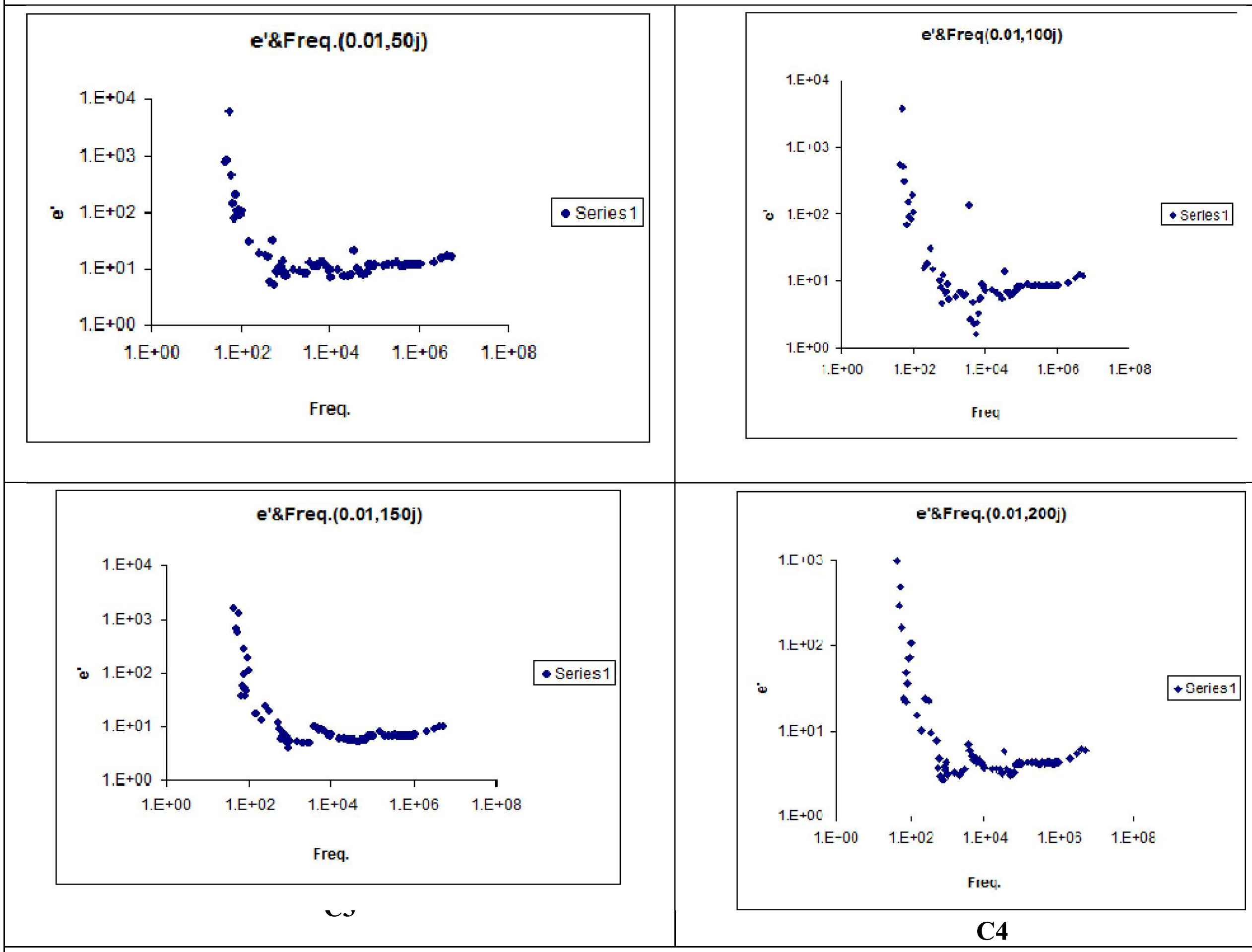

e'&Freq.(0.005,50j)
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
e'
1.E+00 1.E+02 1.E+04 1.E+06 1.E+08
Freq.
Series1

B1


e'&Freq.,(0.005,100j)
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
e'
1.E+00 1.E+02 1.E+04 1.E+06 1.E+08
Freq.
Series1

B2



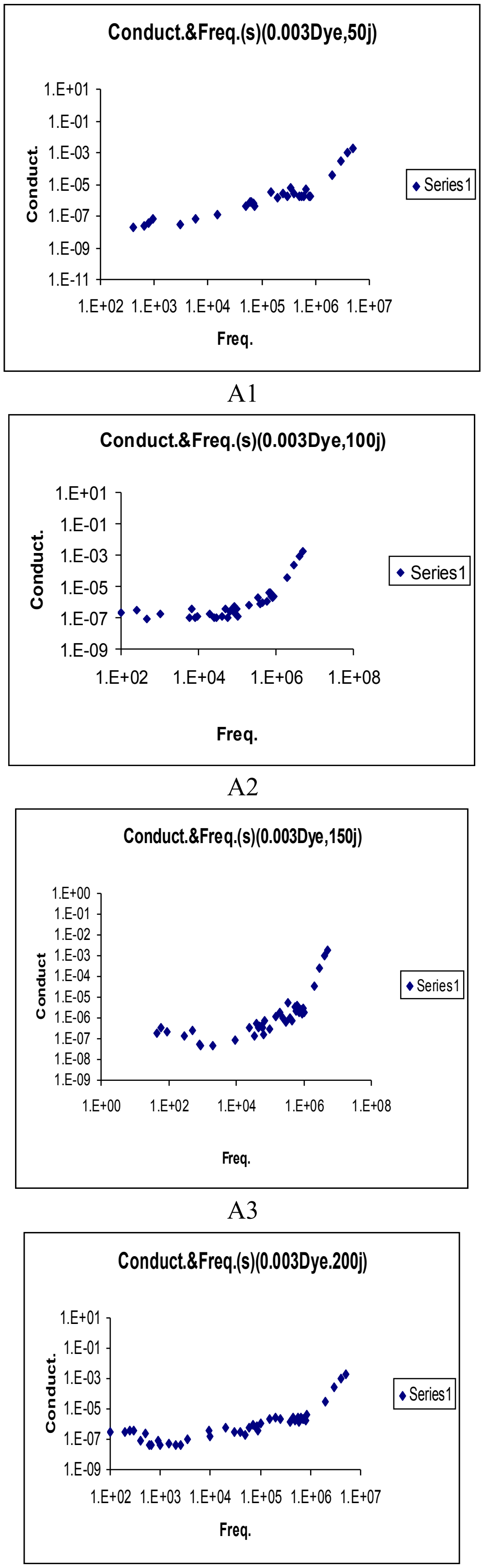


C3

C4

Figure (8c$_{1-4}$)

Figures (8a-c): The dielectric constant of PMMA polymer and PMMA doped with dye concentration (0.003, 0.005 and 0.01wt %) after irradiated with different energy of laser beam during polymerization



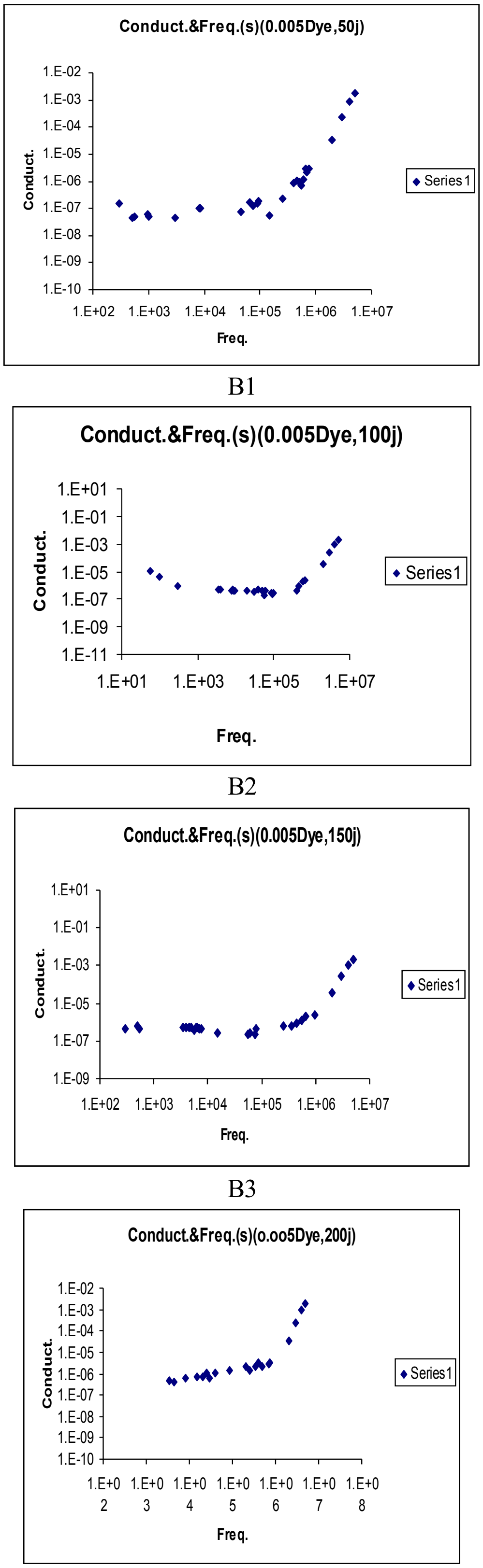
A1

A2

A3

A4

Figure (3.9a$_{1-4}$)



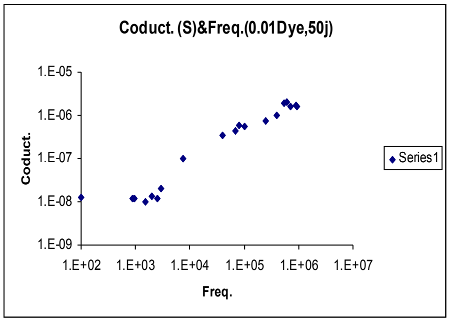
B1

B2

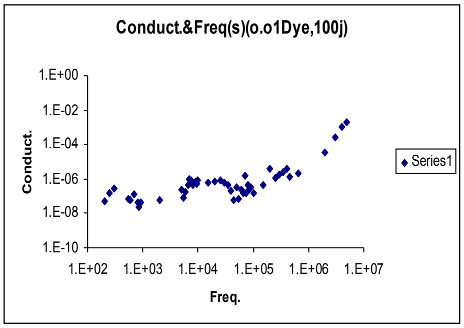
B3

B4

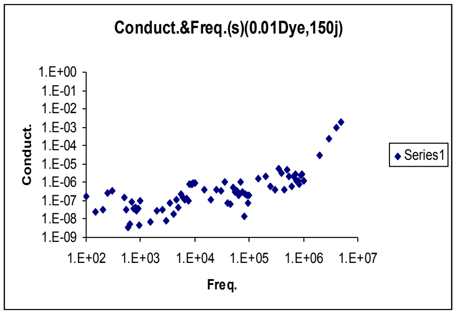
Figure (9b$_{1-4}$)



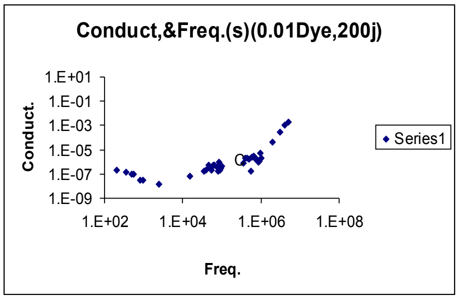
C1



C2



C3



C4

Figure (9c$_{1-4}$)

Figures (9a-c): Conductivities of PMMA polymer and PMMA doped with dye concentration (0.003, 0.005 and 0.01wt %) after irradiated with different energy of laser beam during polymerization

As a function of frequency the conductivities increase slightly with frequency for all samples. Moreover, the dielectric constant drops rapidly with frequency and becomes smaller at higher frequency (=10 KHz) due to the lag of dipole orientation by increasing the applied frequency.

Theoretical studies on comparison materials data using scanning electron photomicrography [25] have shown that in the filler- polymer composite, the filler particles are in the form of the aggregates .The aggregates are separated in the polymer medium. The distance between the aggregates is typically 100A^0 and decreases with increasing loading density.

One can extend this suggestion for the case of PMMA doped with different dye concentrations considering that the matrix consists of alternative conductivities and insulating regions. Figure (10) show that, there are two current components competing with each other in a contact region between conducting regions: one is a current through an internal contact resistance R_C, the other is a current through a contact capacitance C_C .The contact resistance may be the result of a tunneling effect or Ohmic contact effect .R_A represents the resistance with the filler chain region.

At low frequencies, the current flows through the contact resistance since it are blocked at the contact capacitance. The net resistance of the filler chains region is R_C+R_A .At high frequencies; the impedance of the contact capacitance is much lower than the contact resistance and the current flows through the contact capacitance.

Furthermore, since the capacitor impedance is much lower than the resistance, the net resistance at the high frequencies is equal to R_A, which is lower than the net resistance R_C+R_A for the low frequencies .In this way the model of simple RC circuit can explain the behavior of the ac conductivity of PMMA doped polymers.

Let us consider for simplicity that the whole body of doped PMMA polymers can be expressed by a style RC circuit in Figure (10). Consider a cube; 1cm on a side is made of doped PMMA polymer. Two opposite sides of the cube are metallized for electrical contacts. The equivalent circuit between the two plates is assumed to be the RC circuit shown in Figure (11).

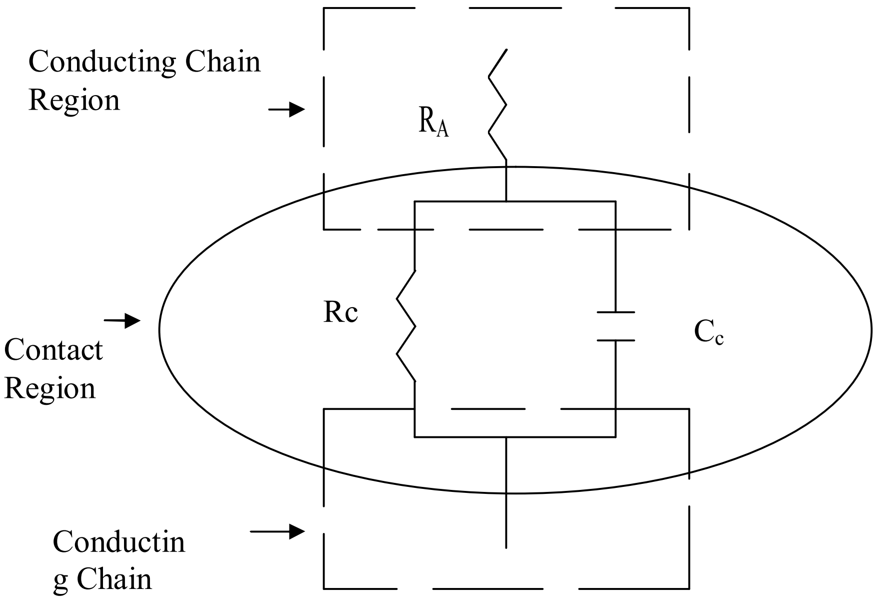


Figure (10): Equivalent resistance –Capacitor circuit in the contact region of conducting chain region. Net resistance at DC= R_A+R_C. Net resistance at high frequency =R_A.

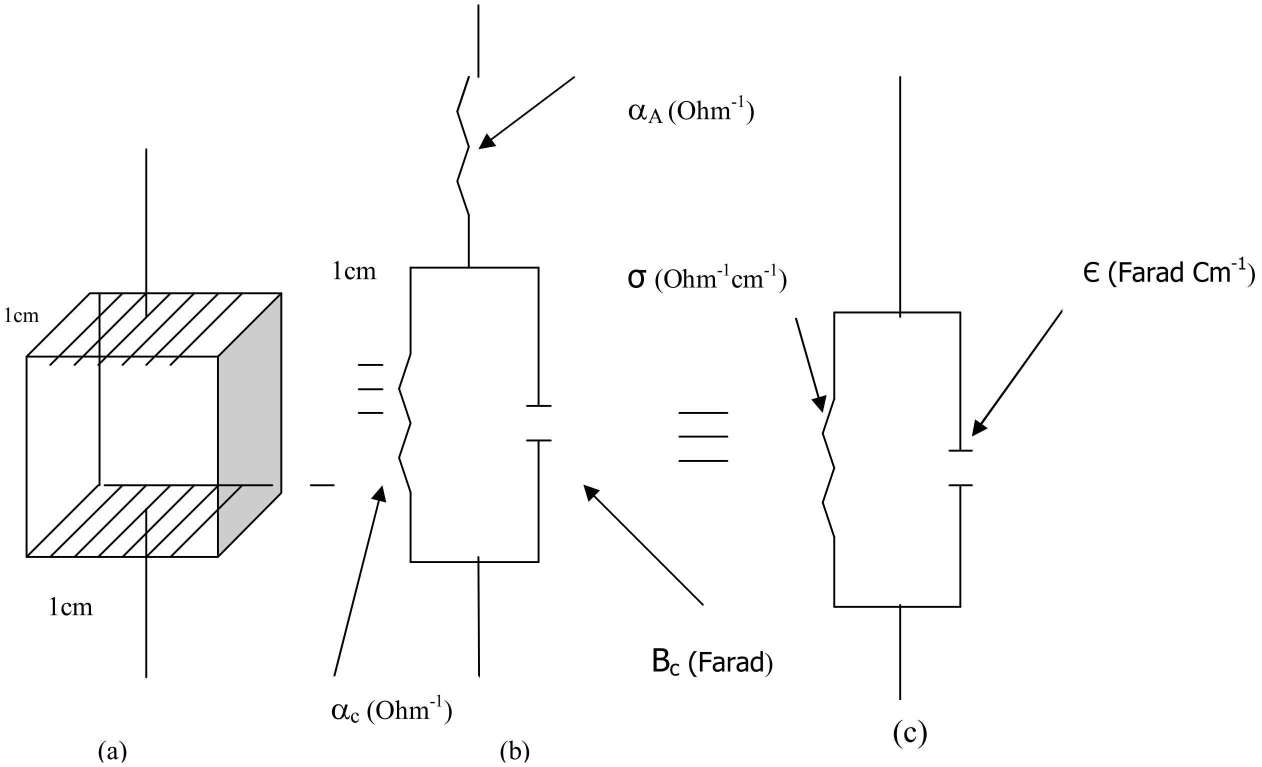


Figure (11): (a) 1cm cube of copolymer, (b) Equivalent circuit, (c) Equivalent circuit in the form of shunt conductance and capacitance.

The three components of the RC circuits are $\alpha_A(\Omega^{-1})$, $\alpha_C(\Omega^{-1})$ and β_C (Farad).The net admittance of the cube sample is

$$Y^{*} = \frac{1}{\frac{1}{\alpha_A} + \frac{1}{(\alpha_C + j\omega\beta_C)}} \qquad (4)$$

Where ω is the angular frequency, letting Y* be:

$$Y^{*} = \sigma + j\omega\varepsilon \qquad (5)$$

The real part σ and the imaginary part ε of the admittance are expressed by:-

$$\sigma = \alpha_A \frac{\alpha_C(\alpha_A + \alpha_C) + (\omega\beta_C)^2}{(\alpha_A + \alpha_C)^2 + (\omega\beta_C)^2} \qquad (6)$$

$$\varepsilon = \beta_C \frac{(\alpha_A)^2}{(\alpha_A + \alpha_C)^2 + (\omega\beta_C)^2} \qquad (7)$$

For the case of 1cm cube, the real part of σ of the admittance is a conductivity of the composite expressed in units of (ohm^{-1}cm^{-1}) and the imaginary part ε is a dielectric constant expressed in terms (F/cm). At low frequency, σ and ε be expressed by:-

$$\sigma_L = \frac{1}{\frac{1}{\alpha_A} + \frac{1}{\alpha_C}} \qquad (8)$$

$$\varepsilon_L = \frac{\beta_C}{(1 + \frac{\alpha_C}{\alpha_A})^2} \qquad (9)$$

At high frequency, σ and ε be expressed by:

$$\sigma_H = \alpha_A \qquad (10)$$

$$\varepsilon_H = \frac{\alpha_A^2}{\omega^2 \beta_C} \qquad (11)$$

Equations (8) to (11) indicate that once the three values σ_L, σ_H and ε_L are determined from experiment, the entire frequency response can be constructed from the conductivity and dielectric constant [25]. From the experimental curves of Figures (8a-c), Figures (9a-c), the three values σ_L, σ_H and ε_L (for all samples) are determined and used to calculate the values of α_A, α_C and β_C which are tabulated in Tables (1a-c). It is noticed from Tables (1a-c) that the values of α_A, α_C and β_C depend on the dye concentration as well as laser energy. PMMA doped with 0.005 (at 200J) dye concentration has higher conductivity values of α_C than other values, meanwhile α_C has nearly a decreasing behavior with laser energy dose for all doped PMMA. Moreover α_C slightly decreases with dye contents. Using these three values, the theoretical values are in good agreement with the experimental data and takes into account the effect of laser beam energy and dye concentrations as clearly observed in Table (1a-c).

Tables (1a-c): The values of α_A, α_C and β_C depend on the dye concentration as well as laser energy Table (1a): The values of α_A, α_C and β_C at 0.003 dye ratio

Energy (Joules)	**σ_H (Ω-1 cm-1)**	**σ_l (Ω-1 cm-1)**	ε_H	ε_L	**α_A (Ω-1)**	**α_c (Ω-1)**	**β_c** (μ Farad)
Pure	9.78E-06	8.61E-09	419.2	1.2	9.78E-06	8.61E-08	1.201058 23.5 MF
50J	0.00201	2.10E-08	67.833	3.41	0.00201	2.10E-08	3.41 $1.2x10^3$ F
100J	0.00176	8.80E-08	72.34	3.39	0.00176	8.80E-08	3.39
150J	0.001948	4.49E-08	15.43	2.988	0.001948	4.49E-08	$2.99x10^6$
200J	0.00186	4.19E-08	57.14	2.14	0.00186	4.19E-08	2.14

Table (1b): The values of α_A, α_C and β_C at 0.005 dye ratio

Energy (Joules)	**σ_H (Ω-1 cm-1)**	**σ_l (Ω-1 cm-1)**	ε_H	ε_L	**α_A (Ω-1)**	**α_c (Ω-1)**	**β_c** (µ Farad)
Pure	0.003	4.37E-07	660.2	4	0.003	4.37E-07	4.001166
50J	0.00177	4.96E-08	15	3	0.00177	4.96E-07	3
100J	0.00187	1.96E-07	30	3.19	0.00187	1.96E-07	3.19
150J	0.0019	2.27E-07	16.94	3.48	0.0019	2.27E-07	3.48
200J	0.00179	6.98E-07	140.75	3.11	0.00179	6.98E-07	3.11

Table (1c): The values of α_A, α_C and β_C at 0.01 dye ratio

Energy (Joules)	**σ_H (Ω-1 cm-1)**	**σ_l (Ω-1 cm-1)**	ε_H	ε_L	**α_A (Ω-1)**	**α_c (Ω-1)**	**β_c** (µ Farad)
Pure	0.012	8.63E-07	231	3	0.0012	8.63E-08	23.5
50J	2.06E-06	1.26e-7	49.1	3.95	2.06E-06	9.88E-09	3.99
100J	0.0197	2.16E-07	16.95	3.2	0.00197	2.16E-08	3.2
150J	0.0188	3.55E-7	68.94	3.26	0.00188	3.55E-08	3.26
200J	0.02	1.42E-07	128.76	3.19	0.002	1.42E-08	3.19

.

Conclusion

From the forgoing results and discussion one may conclude that:

On the one hand, dielectric constant and conductivity of PMMA were influenced by the dye volume fraction. Rgodamine G6 particles produced a rise in conductivity and permittivity and had more influence on samples with high volume fraction. Dielectric singularity was observed at ϕ =0.005 php in the relationship between dielectric constant and composition in the concentration range under study. At ϕ = ϕc ~ 0.005 php, the dielectric constant and ac conductivity of dye/PMMA composite at low frequencies followed the power law model of percolation theory. The dielectric constant of dye/PMMA composites with ϕ >= ϕc was strongly frequency dependent. Above ϕ > ϕc the composites possessed high values of ac conductivity and exhibited nearly weak frequency dependence

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