

## OPTICAL AND A.C. ELECTRICAL PROPERTIES OF PMMA/CB, PMMA/G AND PMMA/(CB+G) COMPOSITES

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Neat PMMA and the PMMA/Carbon Black (CB), and Graphene (G) composites with different loading (PMMA/0.05%(CB), PMMA/0.10%(CB), PMMA/0.15%(CB), PMMA/0.02% (G), PMMA/0.02% (G), PMMA/0.04% (G), PMMA/0.06% (G), PMMA/(0.1%(CB)+0.02%(G) and PMMA/(0.15%(CB)+0.02%(G)) were prepared by dissolving them in the suitable solution and then casted thickness of ~0.3mm. The optical measurements declared that all the prepared samples have an energy gap for the direct allowed transition. The optical energy gap decreases as Carbon black (CB) and Graphene (G) added the PMMA from 5.0 eV to 1.1eV and to 1.0 eV as (CB) and (G) added in the ratio 0.15 and 0.04 % respectively. The transmittance spectra are measured and the optical constants were determined. The measurements showed that the optical constants reveal nonsystematic growing with loading ratio whereas they increase, decrease and return to increase after there. The electrical measurement showed that the A.C conductivity obeys the empirical formula  $\sigma_{a.c}(\omega) = A\omega^s$ , where (s) lies between (0.78-0.0013),  $\sigma_{a.c}(\omega)$  declared frequency-dependent of the neat PMMA and PMMA doped with 0.06 G while it was frequency independent for all composites samples in hole frequency range. The Real and Imaginary Dielectric Constants showed progressive growth with the rise of the loading ratio.

(Received April 19, 2020; Accepted September 14, 2020)

*Keywords:* Optical properties, PMMA, Dielectric properties

### 1. Introduction

The polymers filler composites are receiving increasing interest as a result of unique electrical and optical properties. Poly methyl methacrylate is one of the most important polymers which has been used in various devices [1]. The wide range of applications of (2D) graphene is attributed to the unique properties reflected on the progress of the science communities [2-5]. The large surface area of graphene along with special electrical and thermal properties make it the excellent choice as filler for composites materials graphene has a large surface area and is an Ideal Nano Filler for composites because of the exceptional properties such as thermal and mechanical, along with its Electrical and High Surface Area [6,7]. Carbon Black (CB) is another form of non-crystalline carbon; it is conductive and consists of Carbon at the spherical shape. The most important application of (CB) is a filler to obtain high conductivity polymer composites [8-11]. Carbon black may take introduced substitution in polymer chains or exist as aggregation between polymer chains [12].

The study of optical properties is of great importance, as many researchers have studied the optical properties of materials and polymers in order to manufacture photovoltaic and studying their properties [13,14]. The characterization of optical, electrical properties is a fundamental industrial synthesis of polymeric materials for many applications in optical devices such as filters, total reflectors, polarizers. This paper is comprehensive investigation which contains the results are included the trial measurements of the neat PMMA loaded with different filler like Carbon Black (CB), Graphene (G) at various ratio (PMMA/0.05 % (CB), PMMA/0.10 % (CB), PMMA/0.15 % (CB), PMMA/0.02 % (G), PMMA/0.02 % (G), PMMA/0.04 % (G), PMMA/0.06 % (G), PMMA/(0.1 % (CB) + 0.02 % (G)) and PMMA/(0.15) % (CB) + 0.02 % (G). Also, this work covers optical absorption and energy transport processes take place in undoped and doped thin films. the results and the analysis of the experimental measurements of the neat PMMA loaded with different filler like Carbon Black (CB), Graphene (G) at various ratio (PMMA/0.05%CB, PMMA/0.10%(CB), PMMA/0.15%(CB), PMMA/0.02% (G),

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PMMA/0.02% (G), PMMA/0.04% (G), PMMA/0.06% (G), PMMA/0.1%(CB)+0.02%(G) and PMMA/0.15%(CB)+0.02%(G)). The composites samples prepared using the casting method thickness of  $\sim 0.3$  mm. The Optical Properties were determined using the transmittance spectra in the UV-visible wavelength range (300-1100) nm. The Optical Energy Gap (O.E.G) was estimated using Tauc relation. A number of determining quantities as Optical Energy Gap (O.E.G), Refractive Index, and Dielectric Constant were discussed.

## 2. Results and discussion

The PMMA/CB, PMMA/G optical Properties Composites cast with different loaded ratio times are determined in the range 300–1100 nm.

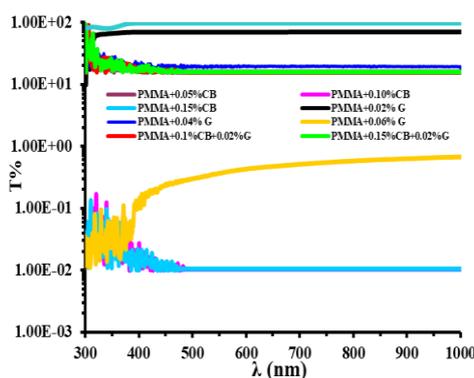


Fig. 1. Transmittance spectra of PMMA/(CB, G) Composites at different ratios.

Fig. 1 show that transmittance spectra of PMMA/(CB, G) composites loaded with different ratio of (CB) and (G). It clear that transmittance of neat PMMA is very high, which shows drastic reduction as carbon black and graphene added separately to the host material in opposite to that the transmittance decreased the wavelength by addition of (G) or (CB) to PMMA. The transmittance returns to increase when the loading was by both filler material (CB+G) and decreases with a further increase of loading ratio. Changes in the level of the transmittance occur with the rise of loading explained according to fact that addition of (CB) and (G) separately or both of making the samples more opaque which intern reduced the transmittance. This attributed to the creation of a new energy level created by (G) or (CB) between the Conduction Band and Valance Band. This level is responsible for the absorption of a photon, which helps electrons to transport in the low energy level in the Energy Gap. In addition, Figure (1) is the highest value transmission of PMMA was (98%) at ( $\lambda = 500$  nm). The Band Gap of the films was measured by Tauc by plot the relation between  $(\alpha h\nu)$  and energy. The plots are shown in Figure (2) for direct allowed ( $r = 0.5$ ) showed the Optical Band Gap of the neat PMMA is 5 eV drastically decreased to low energy especially for (PMMA doped with (CB)).

The reduction in the energy band gap value as seen from the table (1) may be ascribed to an increase in structural disorder of the polymer doped films. The decrease dependence in Optical Energy Gap (O.E.G) on doping may be discussed on the basis of the fact that the incorporation of small amounts of carbon black particles forms free electrons disorder in the host polymer PMMA lattice. The absorption studies have been led to a variety of interesting thin film Optical Phenomenon, which have been thrown considerable light on the band structure of solids and phonic states [15]. The reduction in the band energy gap is also due to carbon black particles dopants incorporated into the polymer chains and, thereby, extending the density of states more into the Visible Region of the Electromagnetic Spectrum as compared to that case of the undoped film. The decrease in the value of the Optical Energy Gap indicates the enhancement of the semiconducting level of the prepared doped films, and existing of the conductive carbon black particles.

The reduction of energy gap related to the increase of Absorption Coefficient which giving rise to shift the Absorption Edge to lower energies as seen from the Table 1. The Energy Gap and Optical Constants have been determined. It is clear the Absorption Coefficient declares significant increase as with different ratios of (G) added to the matrix this attributed to the new energy level

created by ratios of (G) between the Valance Band (V.B) and Conduction Band (C.B). This level it responsible for the absorption of the photon which helps electron to transport in the low energy level in the energy gap. Thus significant reduction will happen in the Optical Energy Gap from 5.0 for neat PMMA to 1.0 eV for PMMA doped with 0.04 (GR) [16].

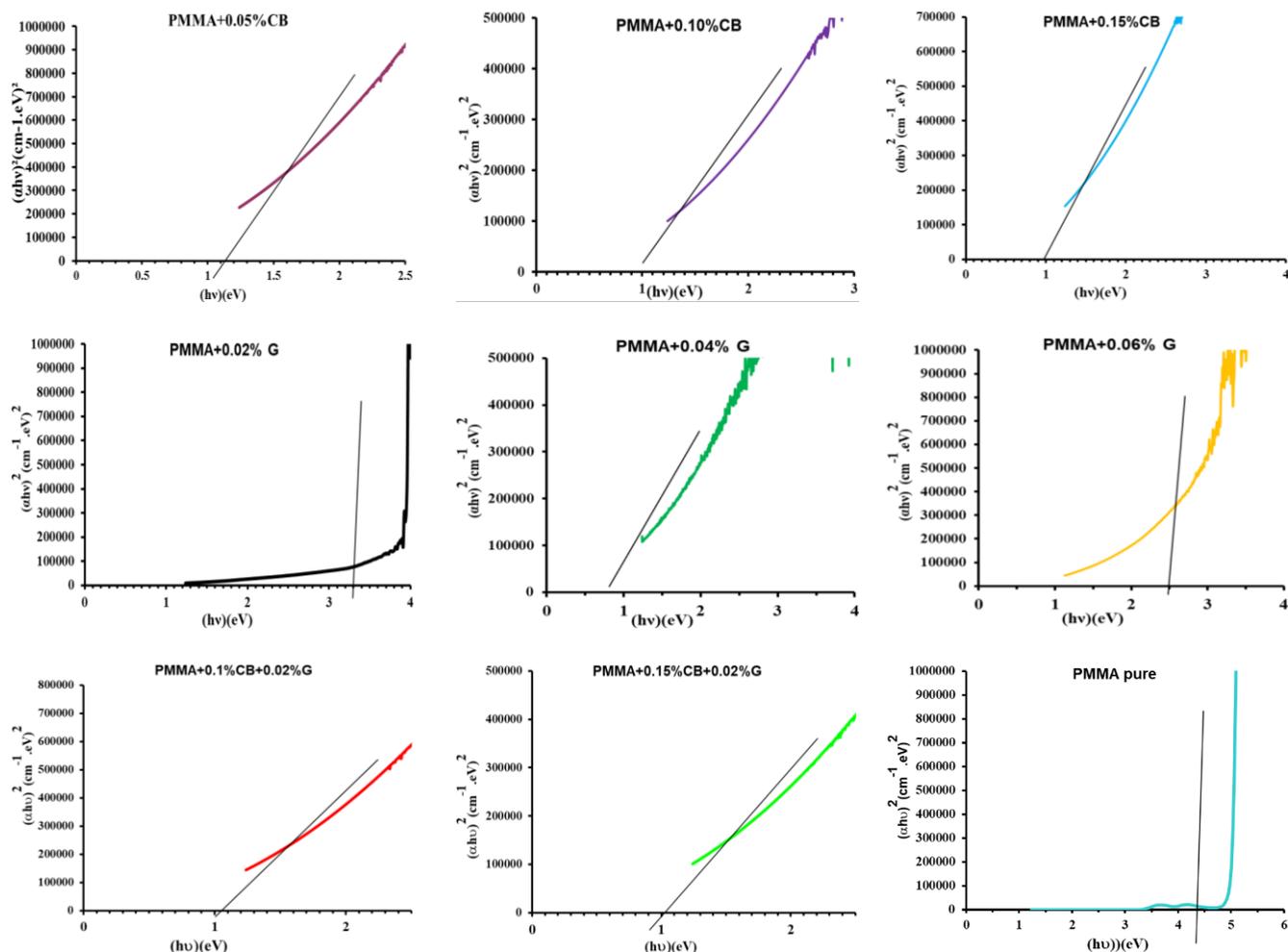


Fig. 2. The variation of  $(\alpha h\nu)^2$  versus  $(\lambda)$  of PMMA/(CB, G) Composites at different loading ratios.

Fig. 3 shown the relationship between the refractive index (n) for PMMA thin film and its composites for PMMA doped with (CB) and (G) in separately, the (n) value was estimated from the equation:

$$n = \left[ \left( \frac{4R}{(R-1)^2} - k^2 \right) \right]^{1/2} - \frac{(R+1)}{(R-1)}$$

and

$k = \frac{\alpha\lambda}{4\pi}$  which relates the refractive index (n) with the absorption coefficient ( $\alpha$ ) and the extinction coefficient (k). Fig. 3 declares that refractive index reduces with increasing the applied wavelength, i.e. dispersion behavior. The refractive index values ranged from (1.23) for PMMA to (1.11) for PMMA doped with (0.1 wt.%) (CB) and (4.07) for PMMA doped with (0.06) (G) calculated at  $\lambda = 500$  nm. The variations of the refractive index with the wavelength reveal that some interactions occur between photons and electrons. Thus it can be proposed that the variation of

refractive index with a variation of the wavelength of the incident light beam takes place due to these interactions [17].

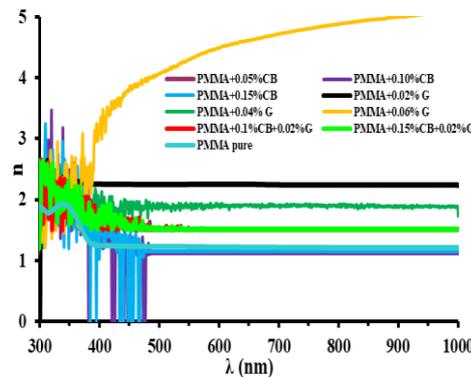


Fig. 3. The variation of  $(n)$  with a wavelength of PMMA/ (CB, G) Composites at different ratios.

The extinction coefficient ( $k$ ) value can be determined from the equation related to the absorption coefficient and wavelength. ( $k$ ) represents the imaginary part of the complex refractive index and it can be defined as the amount of energy loss as a result of interaction between the light and the charge of the medium [24]. The behavior of the extinction coefficient of PMMA/CB, G composites thin films is shown in Fig. 4. The figure shows that the extinction coefficient ( $k$ ) grows with increasing the wavelength, because of the direct relation between ( $k$ ) the absorption coefficient. The value of the extinction coefficient increases with doped 0.1wt.% carbon black because it is directly proportional to the absorption coefficient. Extinction coefficient values exhibit to increase from  $2.82E-06$  to  $1.02E-03$  for PMMA and with 0.1wt.% CB respectively. The growing of ( $k$ ) values are related to various processes like scattering, reflection, and optical absorption occurring on thin-film surfaces [18].

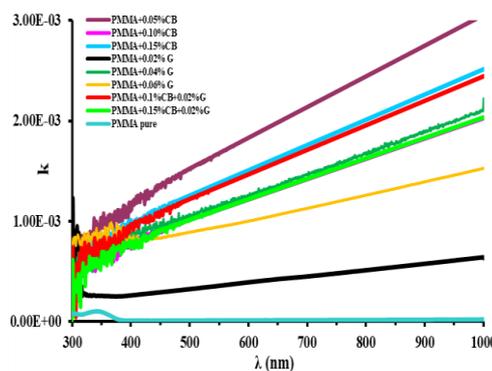


Fig. 4. The variation of  $k$  with the wavelength of PMMA/CB, G Composites at different ratios.

The variation of the imaginary and the reality of the dielectric constant values versus wavelength at (300–1100) nm of PMMA/CB, G composites at various loading ratios are shown in Figs. 5 and 6. The behavior of  $\epsilon_r$  is the same with the refractive index due to the smaller value of  $k^2$  compared with  $n^2$ , while  $\epsilon_i$  is based on the  $k$  values. It is found that  $\epsilon_r$  increase as CB and G added to PMMA, then decrease and return to increase fro-high loading ratio. Moreover,  $\epsilon_1$  is found to increase from 1.52 to 2.29 and to 2.25 when CB and G added to PMMA.

The imaginary part of dielectric constant  $\epsilon_2$  showed the same behavior of  $k$  with loading ratio. Table 1 included that  $\epsilon_2$  of PMMA/CB, G Composites increases from  $6.95E-06$  to  $2.26E-03$

as CB added to PMMA at 0.1%, also  $\epsilon_2$  increases from 6.95E-06 to 1.81E-03 as G added to PMMA at 0.15%. Value of  $k$  and  $n$  can give to  $\epsilon_r$  and  $\epsilon_i$ .

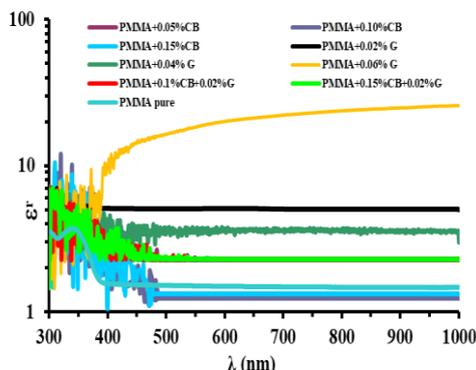


Fig. 5. The variation of  $\epsilon_r$  with the wavelength of PMMA/CB, G Composites at different ratios.

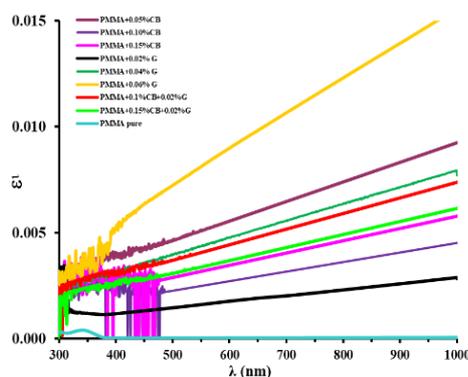


Fig. 6. The  $\epsilon_i$  variation with wavelength of PMMA/CB, G Composites at different ratios.

Table 1. Values of  $\epsilon_r$ ,  $n$ ,  $\epsilon_i$ ,  $k$ ,  $T$  at  $\lambda=500\text{nm}$ , and  $E_g^{opt}$  of PMMA/CB, G composites at different ratios.

| Sample              | T%    | $\alpha$ ( $\text{cm}^{-1}$ ) | $k$      | $n$  | $\epsilon_r$ | $\epsilon_i$ | $E_g$ (eV) |
|---------------------|-------|-------------------------------|----------|------|--------------|--------------|------------|
| PMMA+0.05%CB        | 15.84 | 76.77                         | 3.06E-04 | 1.51 | 2.29         | 9.24E-04     | 1.20       |
| PMMA+0.10%CB        | 0.01  | 400310.09                     | 1.02E-03 | 1.11 | 1.24         | 2.26E-03     | 1.25       |
| PMMA+0.15%CB        | 0.01  | 38400.90                      | 3.15E-04 | 1.15 | 1.32         | 7.24E-04     | 1.10       |
| PMMA+0.02% G        | 0.69  | 3.02                          | 8.14E-05 | 2.25 | 5.07         | 3.66E-04     | 3.90       |
| PMMA+0.04% G        | 19.80 | 16785.16                      | 2.08E-04 | 1.92 | 3.67         | 7.97E-04     | 1.00       |
| PMMA+0.06% G        | 0.30  | 19182.92                      | 2.22E-04 | 4.07 | 16.55        | 1.81E-03     | 3.00       |
| PMMA+0.1%CB+0.02%G  | 61.41 | 23196.83                      | 2.44E-04 | 1.51 | 2.29         | 7.39E-04     | 1.15       |
| PMMA+0.15%CB+0.02%G | 50.87 | 15916.19                      | 2.03E-04 | 1.54 | 2.36         | 6.22E-04     | 1.17       |
| PMMA pure           | 98.04 | 0.71                          | 2.82E-06 | 1.23 | 1.52         | 6.95E-06     | 5.00       |

The variation of  $\sigma_{ac}(\omega)$  as a function of the frequency of PMMA/CB, G composites at different ratios are plotted in figure (7). It is obvious that  $\sigma_{ac}(\omega)$  is frequency independent in the hole frequency range  $25 \times 10^3 - 5 \times 10^6 \text{Hz}$ , this is attributed to domination of D.C conductivity where the polarization is slightly changed i.e.  $\sigma_{ac}(\omega)$ , while it is frequency-dependent for pure PMMA as well as for (6% GR) composite, i.e. the conductivity is pure A.C, this is resulting from the electronic polarization. The exponential factor ( $s$ ) were obtained from the plotting of  $\ln(\sigma_{tot}(\omega))$  versus  $\ln(\omega)$  PMMA/CB, G composites at different ratios. Table (2) show the values of  $s$  are very low for all composites samples. This gives an indication that conductivity takes place throughout hopping, on the other hand, the exponent  $s$  vary with changing of filler content, the increase of  $s$  attributed to the increase of charges carriers accompanied the addition of graphene and CB but in

less extent, while the decrease of  $s$  attributed to formation of immiscible blends. The results showed  $\sigma_{tot}(\omega)$  increases with the increase of frequency from  $25 \times 10^3 - 5 \times 10^6$  Hz.

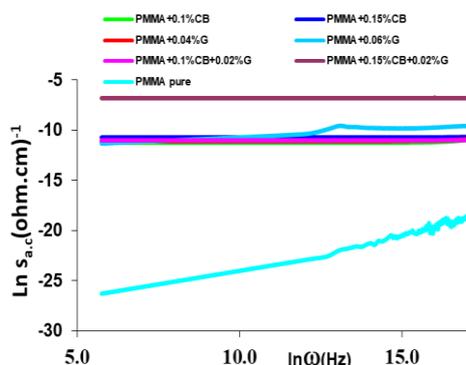


Fig. 7. The variation of  $\ln(\sigma_{a,c})$  with  $\ln(\omega)$  of PMMA/CB, G Composites at different ratios.

Table 2. Illustrates  $s$  values for PMMA/CB, G Composites at different ratios.

| Samples             | S (value) |
|---------------------|-----------|
| PMMA+0.1%CB         | 0.077     |
| PMMA+0.15%CB        | 0.013     |
| PMMA+0.04%G         | 0.0472    |
| PMMA+0.06%G         | 0.1145    |
| PMMA+0.1%CB+0.02%G  | 0.0138    |
| PMMA+0.15%CB+0.02%G | 0.0013    |
| PMMA pure           | 0.7852    |

A Debye-type relaxation is obtained by plotting the curves  $\epsilon_r$  versus  $\ln(\omega)$  and  $\epsilon_i$  versus  $\ln(\omega)$  which were shown in Figures (8 and 9).

The dielectric constant ( $\epsilon_r$ ) for PMMA/CB, G Composites at different ratios were measured within the employed frequency range ( $2.5 \times 10^3 - 5 \times 10^6$  Hz), from the spectrum of  $\epsilon_r$  versus  $\ln(\omega)$  it is obvious that ( $\epsilon_r$ ) exhibit to increase in a progressive manner with increase filler content, while  $\epsilon_r$  tends to decrease with high frequency to below values, the electrode blocking is affected by the electrode polarization, but the frequency the dielectric signal is don't have related with electrode polarization, moreover (at frequency = 50 Hz)  $\epsilon_r$  increasing of pure PMMA from (0.09) to (12784) for PMMA + 0.15 % CB + 0.02%G composite sample. The increase of ( $\epsilon_r$ ) with increasing of graphene and CB in composites samples ascribed to the increase of the charge carriers because of additional conductive material.

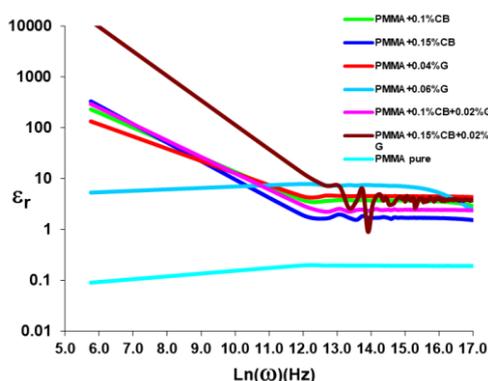


Fig. 8. The variation of  $\epsilon_r$  with  $\ln(\omega)$  of PMMA/CB, G Composites at different ratios.

Fig. 9 showed the variation of ( $\epsilon_i$ ) with the frequency of PMMA/CB, G Composites at different ratios. ( $\epsilon_i$ ) become high with a high level of graphene and CB in composites samples, indeed ( $\epsilon_i$ ) increases from 0.139 for pure PMMA to  $4 \times 10^6$  for PMMA+0.15%CB+0.02%G. It is obvious from the spectrums of all composites are empty from any relaxation peaks at the whole frequency range while PMMA declares those.

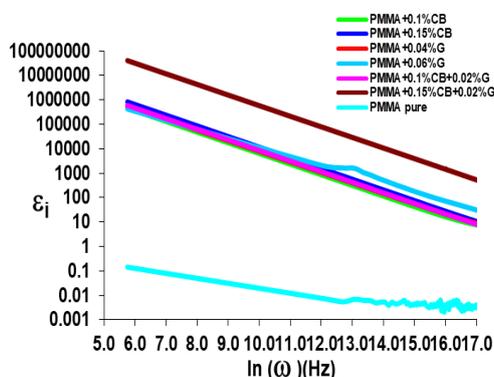


Fig. 9. The variation of  $\epsilon_i$  with  $\ln(\omega)$  of PMMA/CN, G composites at different ratios.

### 3. Conclusions

PMMA/CB, G composites become more opaque with the increase of loading ratio by increasing the density and changing of the energy level of the absorption to be low level. Minimum energy gap (1.0 eV) obtained for PMMA+0.04% G composite sample. Maximum refractive index obtained for PMMA+0.06% G composite sample.

All the optical parameters of neat PMMA like  $n$ ,  $k$  real and imaginary dielectric constant is lower than those of composites samples, while the energy gap of PMMA is higher than those of composites samples. The loading process of PMMA with different types and ratio of filler is done successfully. The conductivity is pure A.C for PMMA while it is frequency independent for all composites samples.

The values of ( $\epsilon_r$ ) and ( $\epsilon_i$ ) clearly affected by the increasing of graphene and CB content. The exponent  $s$  was very low for all composites samples. All the composites samples reveal no relaxation peaks in the used frequency range. The project of this work was succeeded by increasing the conductivity of PMMA four orders of magnitude.

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