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Dopping Effect On Optical Constants of Polymethylmethacrylate (PMMA)

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Abstract

The optical constants (refractive index (n) , extinction coefficient (k) , real and imaginary parts of dielectric constant(ε_1&ε_2)) of polymethyl methacrylate (PMMA) doped with methylene blue (mb) and methyl red (mr) with thickness in the range (0.1-0.2) mm were measured in the wavelength range (200-900) nm. Refractive index (n) and extinction coefficient (k) showed irregular changes with increasing (mb) dopant concentrations, while (n) and (k) of PMMA doped with (mr) declared a systematic increase with increasing dopant concentrations. The data showed that (n) values of PMMA doped with (mr) are lower than the values of samples doped with (mb) which is atteributed to the progressive increase of absorbance in the wavelength range (400-550) nm with increasing (mr) concentration .

Keyword: Optical Constants , Polymethylmethacrylate(PMMA)

تأثير التطعيم على الثوابت البصرية للبولي مثيل ميثا اكريلايت

الخلاصة

تم حساب الثوابت البصرية (معامل الانكسار (n) ,معامل الخمود(k) وثابت العزل الحقيقي (ε_1) والخيالي (ε_2)) للبولي مثيل ميثا اكريلايت (PMMA) المطعم بالمثيل الازرق (mb) والمثيل الاحمر (mr) وبسمك mm (0.1-0.2) وضمن مدى الطول الموجي nm (200-900) ,معامل انكسارومعامل خمود (PMMA) المطعم بالمثيل الازرق اظهر تغيرا غير منتظما مع زيادة تركيز التطعيم بينما اظهر معامل انكسار ومعامل خمود (PMMA)المطعم بالمثيل الاحمر زيادة منتظمة مع زيادة تركيز التطعيم . أظهرت القياسات أن قيم (n) لنماذج (PMMA) المطعم بالمثيل الاحمر اوطأ من تلك التي تعود لنماذج (PMMA) المطعم بالمثيل الازرق والذي يعزى الى الزيادة المستمرة في الامتصاصية مع زيادة تركيز المثيل الاحمر في مدى الطول الموجي nm (400-550) .

Introduction

Polymeric substances make up the most important class of organic materials , technically and economically . The familiar plastics , fibers , elastomers and biological materials that surround us attest to this importance .Such substances , which are composed of great many identical groups or repeating units , are known as (high polymers) . Polymers composed of more than one kind of repeating units are termed copolymers [1] . It is well known that polar polymers in solution are divided into two groups according to their dielectric behavior [2,3] .The first group exhibits a

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dielectric absorption in low frequency region [10^1-10^6 Hz] , the second group exhibits a dielectric absorption in the high frequency region [10^6-10^{12} Hz] . Polymethyle methacrylate belongs to this group [4,5]. The methacrylate ester polymers are exceptionally clear, hard, glass plastics .They soften at temperature over 212 F ^{o}, this permits fabrication by molding and extrusion techniques but limits uses to those involving only moderate temperatures PMMA is widely used sometimes with plasticzer and or small amount of other ester as copolymers. The resins are so widespread under the trade name of plexiglas in United States and Perspex in Europe that these words have become synonmous to transport plastic panels, windows and windshields. The resistance of these resins to shattering and to weather has led to their large scale application in aircraft [1]. Colorant of plastics include a wide variety of inorganic and organic materials leading to transparent colored products when incorporated into transparent plastics which are normally carried out by adding colorant to the powdered plastic. Tumbling and compounding on hot rolls or in extruder, colored casting of PMMA are produced by dissolving or dispersing the colorants in the syrup before polymerization [6,7].

PMMA films were prepared by the slow evaporation of polymer solution by Liu and Guillet [8].Films with specific weight ratio of PMMA were obtained by addition of PMMA to a known concentration of methylene chloride. The solution was transferred in a-2 inch diameter culture covered and left in dark over night ,then the films were annealed at 114 C^0 under vacuum for 6 hours .Papanu et al [9] used chlorobenzen as a solvent to prepare PMMA films .The polymer solution was spin coated on to silicon (Si) wafers previously cleaned .The samples were baked at 160 C^0 for 1 hour in a convection oven and then quenched at room temperature. PMMA films were prepared on polystyrene (PS) substrate by Sferraza et al [10] ,Wang et al [11]and Higgins et al [12].It was pointed out by Seeman et al [13] that the stability of the prepared films is relating on the type of the substrate and on the films thickness.

The purpose of this work is to study the effect of additives on the optical constants of glassy polymer .The polymer used is polymethyl methacrylate PMMA with additives methylene blue (mb) and methyl red (mr) with different concentrations. Solutions of polymer with different concentrations of (mb)and (mr) were prepared by addition of PMMA to a known concentration of methylene chloride. PMMA films were obtained using casting method. This study takes into account the resultant changes in these constants.

Basic Considerations:-

The optical behavior of materials are utilized to determine their optical constants (refractive index (n), extinction coefficient (k) , real and imaginary parts of dielectric constants (ε_1 , ε_2)). Several methods were proposed to determine the optical constants , they involve spectrophotometric measurements of reflectance (R) and transmittance (T)

of sample in the wavelength range [14,15].
The extinction coefficient (imaginary part of the refractive index) can be calculated by the relation [16]:

$$k = \frac{a\,l}{4p} \qquad (1)$$

where l is the wavelength , a is the absorption coefficient which can be obtained using the following equation [17]:

$$a = \frac{2.3\,log\left(\frac{1}{T}\right)}{x} \qquad (2)$$

where T is the transmittance.
x is the thickness of sample .
The refractive index (n) can be measured (when the reflectance (R) and (k) are known) by using the equation [17] :

$$n = \sqrt{\frac{4R}{(R-1)^2 - k^2} - \frac{(R+1)}{(R-1)}} \qquad (3)$$

The complex index ($\overline{N}$) is given by [10]:

$$\overline{N} = n - ik = \sqrt{e} \qquad (4)$$

where ε is the complex dielectric constant , given by:

$$e = e_1 - ie_2 \qquad (5)$$

The parameter ε_1 is the real part of dielectric constant , ε_2 is the imaginary part of dielectric constant .From equs (4) and (5) one can obtain :

$$e_1 = n^2 - k^2 \qquad (6)$$

$$e_2 = 2nk \qquad (7)$$

Experimental Part:-

Polymethyl methacrylated (PMMA), supplied by ICI company in the form of granules were used as matrix .Methylene chloride, supplied by BDH Company of purity 99.99 , was used as solvent . As a dopant , methylene blue (mb) and methyl red (mr) ,supplied by Merck Company with molecular weigh ($\overline{m}$ W) (319.85 and 269.30) respectively were used . PMMA grains of weight (0.6) gm were dissolved in (10) Vl of methylene chloride (CH_2Cl_2) to obtain solution of 6% wt.\wt. . The solution was shaken well by hand for (1/2) hour or more to obtain homogenous contents , (3ml) of the prepared solution was then transferred into clean glass Petri dish of 6 cm in diameter placed on a platform which can be leveled with the aid of spirit level fixed on the platfrom for drying cycle . The whole unit was kept inside an oven at temperature ($50C^o$) for at least 2 hours, and then left to cool slowly to room temperature . The dried films were then removed easily using tweezers clamp.
Several experiments were done on film casting in order to ensure dried samples without bubbles and thermal damage . The thickness of prepared films was measured between (0.1 - 0.2) mm .
Films doping was performed by dissolving mr and mb pigments in the solution of methylene chloride of concentration (6% wt./wt.). The chosen concentrations of dopants relative to pure PMMA in (wt./wt.) were (0.01, 0.015, 0.1 and 0.15). The measurements of absorbance and transmittance spectra in the wavelength range (200-900) nm were carried out using UV/160/Shimadzu

Spectrophotometer which has full scale absorbance up to 2.5.
The absorption coefficient and extinction coefficient were calculated using equs (1&2) .The variation of the refractive index as function of wavelength was obtained by using equ. (3). The real and imaginary parts of dielectric constants ε_1 and ε_2 were calculated by using equs.(6) and (7).

Results and Discussion :-

The refractive index (n) of pure and doped PMMA with mb were determined using equ. (3) . Fig(1a) shows the variation of (n) as function of wavelength (l) . It is clear that (n) of pure PMMA decreases with (l) , however(n) increases in the l range (200-360)nm.
In order to compare our results of (n) of pure PMMA with published data , which were calculated at l =600 nm the value of (n) was found (2.13) for thickness of (0.1-0.2) mm , while Papanu et al [9] obtained (n) value =1.48 of PMMA thin films with thickness of 1000 nm deposited on silicon wafer (Si) .Also Wyart and Daillant [18] reported n=1.49 for PMMA of thickness (30-45) nm deposited on glass .The difference in (n) values is attributed to difference in thickness .
On the other hand, one can observe that (n) of doped PMMA increases with increasing l and there is irregular variation of (n) with increasing mr concentrations , indeed (n)changes from 4.03 to 5.57 at l =600 nm (see table(1)) when mb concentration increases from 0.01 to 0.15 wt. % . Another noticeable remark the refractive index pattern of doped PMMA exhibited minimum value located at l =660 nm .However curve of n of PMMA doped with 0.015 mb showed two minimum values at l =660 ,780 nm, these minimum values of (n) of different mb concentrations result from high photosensitivity of mr at the forementioned wavelength range [19] .
Fig.(1b) shows the relation between the refractive index as function of wavelength for pure and doped PMMA with mr of different concentrations . In this figure,(n) exhibits to increase with l at (0.1, 0.015) wt.% doping concentrations . On the other hand (n) showed a systematic increase with increasing mr concentrations . Moreover, (n) increases from 2.13 to 3.91 (when mr concentration increases from (0 to 0.10) wt.% ,but at 0.15 mr concentration (n) terminated its decreases .As in PMMA doped with mb the refractive index also shows a decreasing region in the l range (400-550) nm which is analogous to valley results from high absorbance of mr atoms which take place in this wavelength range [19] .
In general, it is clear that (n) values of samples doped with mr are lower than values of samples doped with mb, this means that the former samples are more transparent than the latter .
The dependence of extinction coefficient (k) on the wavelength obtained using equ.(1) is shown in Fig.(2a& b) for pure and doped samples . It is noticed that(k) value of pure sample has reduced , becomes smaller at the region near the absorption edge , and becomes very small with increasing l , while (k) for doped sample with mb Fig .(2a), shows an increase with

increasing l .The maximum peaks belong to maximum absorption of mb [19] , on the other hand (k) exhibits slightly random changes with increasing mb concentrations, indeed (k) changes from $2.79x10^{-5}$ to $3.0817x10^{-4}$ when mb concentration increases from (0-0.15) wt.%, (see table(1)) .Also the contrast of relation between(n) and (k)is clearly observed .

Fig .(2b), shows the variations of (k)with l of pure and doped PMMA with mr . (k) shows an increase of one order of magnitude with increasing dopant concentration , moreover k increases from $2.79x10^{-5}$ to $2.974x10^{-4}$ when mr concentration increases from (0-0.15)wt.% .The behavior of (k) can be ascribed to high absorption coefficient [16 , 20] .This result indicates that the dopant atoms of mr will modify the structure of the host polymer[21]. An interesting result is mr dopants increases the absorbance in the visible region , especially in l range (400-600) nm .Moreover , the sudden increase in(k) values shifts to longer l when mr concentration increases from (0.01 to 0.015) wt.% .

The real and imaginary parts of dielectric constants $\varepsilon_1$and ε_2 of pure and doped PMMA with mb and mr with different concentrations were calculated by using equations (6) and (7) . The dependence of ε_1 and ε_2 on l are shown in Figs. (3a&b , 4a & b) . It is concluded that the variation of ε_1 mainly depends on (n^2) because of small values of (k^2), while ε_2 mainly depends on the (k) values which are related to the variation of absorption coefficients.

Conclusions:-

We successfully prepared films samples of pure and doped PMMA with mb and mr with different concentrations which were used for measurements of optical constants . The refractive index (n) and extinction coefficient (k) of pure PMMA showed a decrease with wavelength while(n) for doped PMMA with mb declared a non systematic variation with doping concentrations in contrast with the behavior of (n) for PMMA doped with mr which showed a regular variation .Increasing of mb concentrations did not always reflect an increase in the absorbance and consequently in(k) values as in PMMA doped with mb, while (k) of PMMA doped with mr declared progressive increase with increasing dopant concentrations .

The lower (n) values of PMMA doped with mr compared with those of PMMA doped with mb means that mr is a more favorable dopant than mr.

References:-

1. Siman O. , Parkinson W.W. and Bobb C.D . , Radiation Effects on Organic Materials ,8, 127 ,(1969) .
2. Stock Mayer W. H ., Pure and Appl .Chem. , 15 , 532 , (1967) .
3. Bates T . , Ivin K . J . and Williams G . , Trans. Faraday Soc. , 3 , 4 ,(1967) .
4. De Brouckere L ., Buess D ., J . de Bock and Versluys J . , Bull Soc. Chem. , Belg. , 64 , 669 , (1955) .
5. De Brouckere L., Buess D. , and , Van Beek L. K. H., J. Polym . Sci , 23 , 233 , (1957).

6. Billmeyer F. W. , Text Book of Polymer Science , 3rd ed. John Wiley and Sons , (1984) .
7. Encyclopeiedia of Polymer Science and Technology , John Wiley , 9, 525 , (1988).
8. Liu G. and Guillet J.E., Macromolecules,23, 1393, (1990).
9. J.S. Popanu , D.W. Hess , D. S. Soane and A. T. Bell , Polym . Sci. , 39 , 303, (1990) .
10. Sferrazza M., Heppenstall-Butler M., Gubitt R., Bucknall D., Webster J., Jones R.A.L, Phys. Rev. Lett., 81, 5173 (1998).
11. Wang C., Krausch G., Geoghe an M,. , Langmuir 17,6269 (2001).
12. Higgins A.M., Sferrazza M., Jones R.A.L., Jukes P.C, Sharp J.S., Dryden L.E., Webster J., Eur.Phys.J.E 8,137(2002)
13. Seemann R., Heringhaus S., Jacobs K., Phyus. Rev. Lett.86, 5534(2001)
14. Minkov D. A. , J. Phys . D: Appl. Phys. , 22 , 199, (1989) .
15. Manifacier J. , Gasiot J. and Fillared J. , J. Phys. E, Sci. Instrum. , 9, 1002 ,(1976).
16. Pankov J. , Optical Processes in Semiconductors, London , (1971).
17. Mott N. and Davis E., Electronic Process in Non-Crystalline Materials, 2nd Edtion, University Press, Oxford , (1979) .
18. Wyart F. B. and Daillant F., J. Phys ., 68 , 1084 ,(1990).
19. Gordon P. F. and Gregory P. , Organic Chemistry in Colour , Springer Verlag Berlin, (1983).
20. Bertie J. E., Hand Book of Vibrational Spectroscopy ,John Wiley and Sones , (2001).
21. Gonzalez J. M., Marquez E. and Petrovic D. M., Physica Scripta, 55, 108, (1997).

Table (1) Illustrates the values of(n, k , ε_1 and ε_2) at l =600 nm of pure and doped PMMA with mb with different concentrations .

Doping Concentrations	n	k	ε_1	ε_2
PMMA+0.0 mb	2.13	$2.792\text{x}10^{-5}$	4.54	$1.191\text{x}10^{-4}$
PMMA+0.01 mb	4.03	$4.057\text{x}10^{-4}$	16.27	$3.272\text{x}10^{-3}$
PMMA+0.015 mb	5.79	$3.300\text{x}10^{-4}$	33.55	$3.823\text{x}10^{-3}$
PMMA+0.1 mb	2.66	$4.306\text{x}10^{-4}$	7.08	$2.291\text{x}10^{-3}$
PMMA+0.15 mb	5.57	$3.082\text{x}10^{-4}$	30.98	$3.431\text{x}10^{-3}$

Table(2) Illustrates the values of (n ,k $\varepsilon1$and $\varepsilon2$) at l =600 nm of pure and doped PMMA with mr with different concentrations .

Doping Concentrations	n	k	ε_1	ε_2
PMMA+0.0 mr	2.13	$2.792\text{x}10^{-5}$	4.54	$1.191\text{x}10^{-4}$
PMMA+0.01 mr	2.14	$2.698\text{x}10^{-5}$	4.57	$1.153\text{x}0^{-4}$
PMMA+0.015 mr	3.89	$6.984\text{x}10^{-5}$	15.13	$5.432\text{x}10^{-4}$
PMMA+0.1 mr	3.91	$2.275\text{x}10^{-4}$	15.28	$1.779\text{x}10^{-3}$
PMMA+0.15 mr	3.56	$2.974\text{x}10^{-4}$	12.68	$2.118\text{x}10^{-3}$

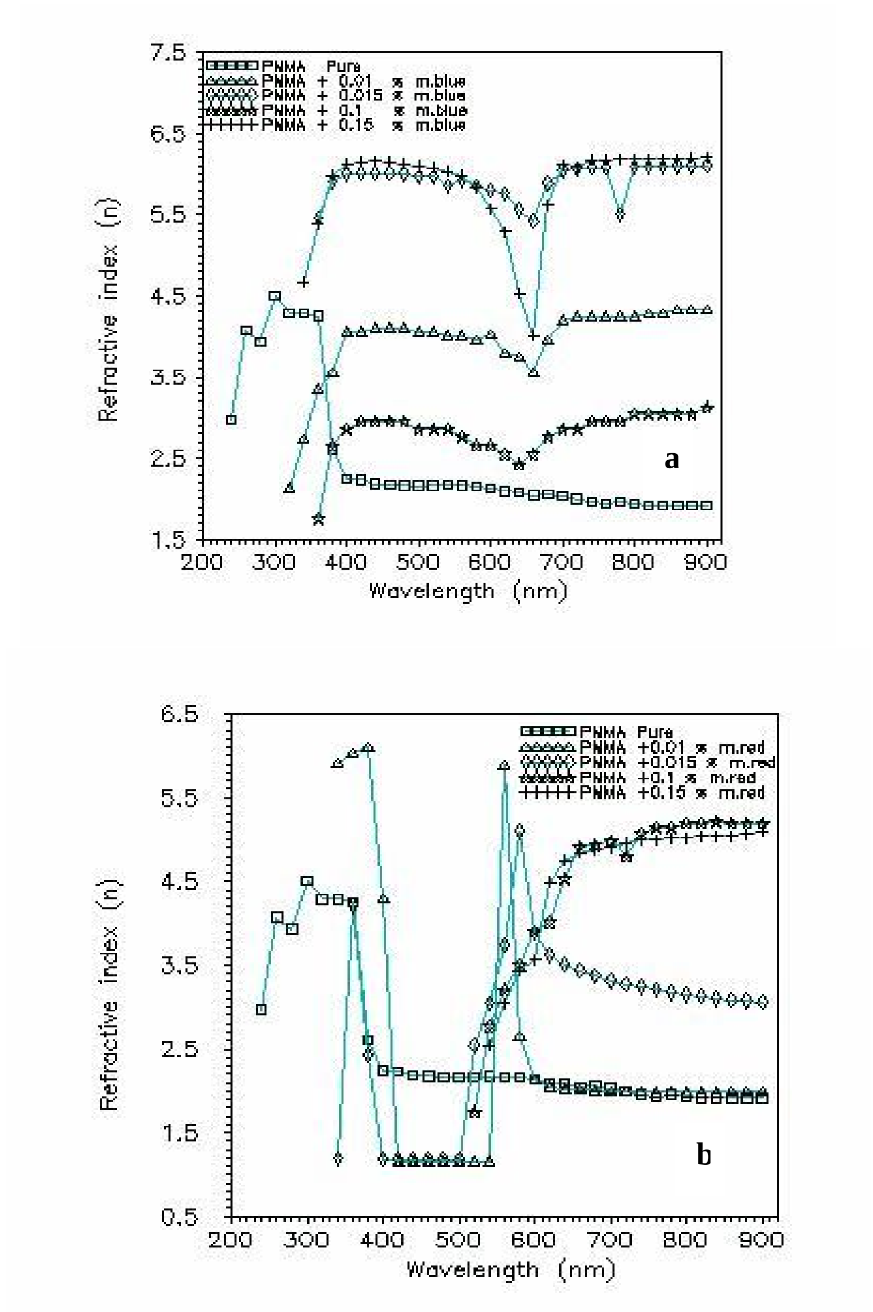


Fig.(1) Variation in refractive index (n) as function of wavelength of pure and doped PMMA with: (a) mb with different concentrations, (b) mr with different concentrations.

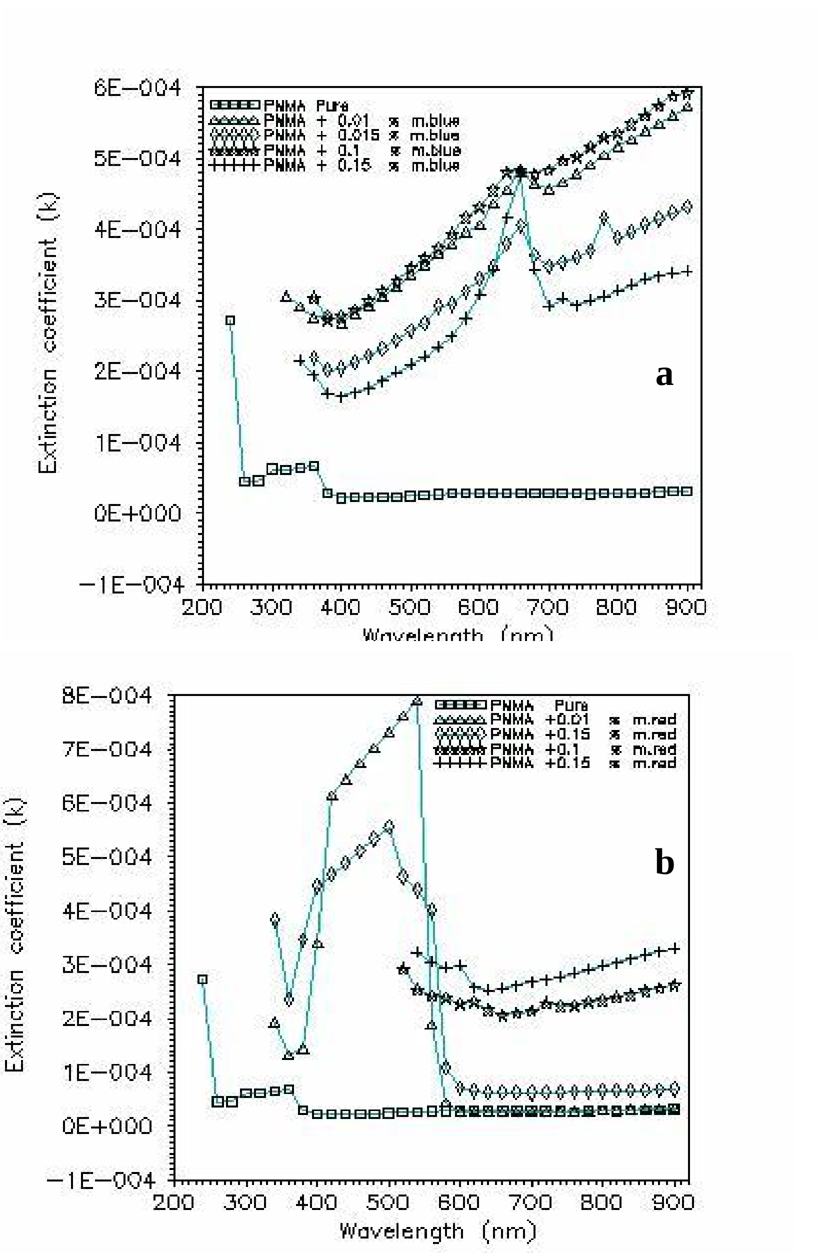
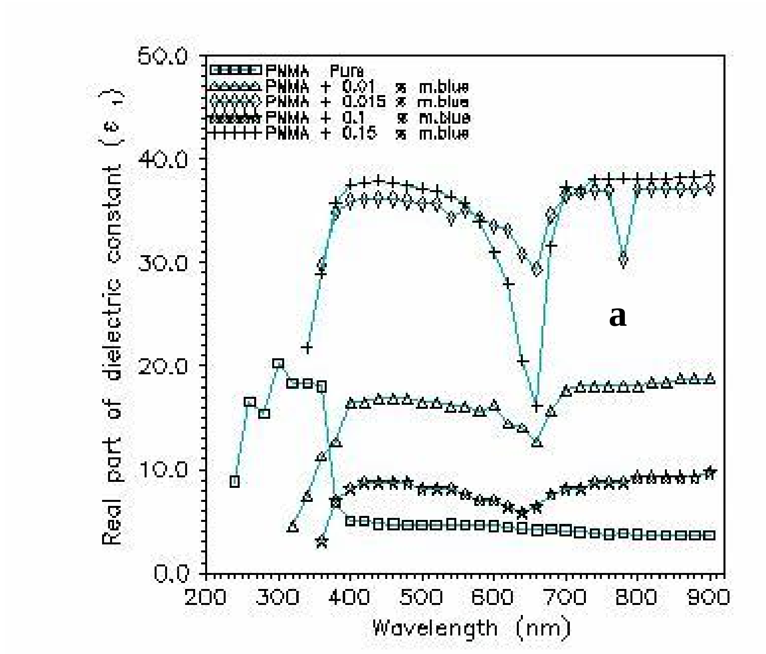


Fig.(2) Variation in extinction coefficient (k) as function of wavelength of pure and doped PMMA with: (a)mb with different concentrations ,(b)mr with different concentrations.



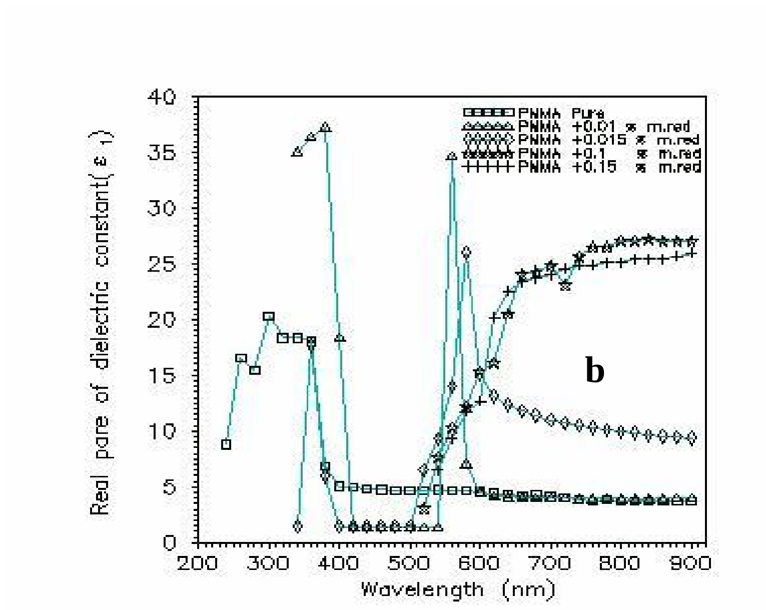
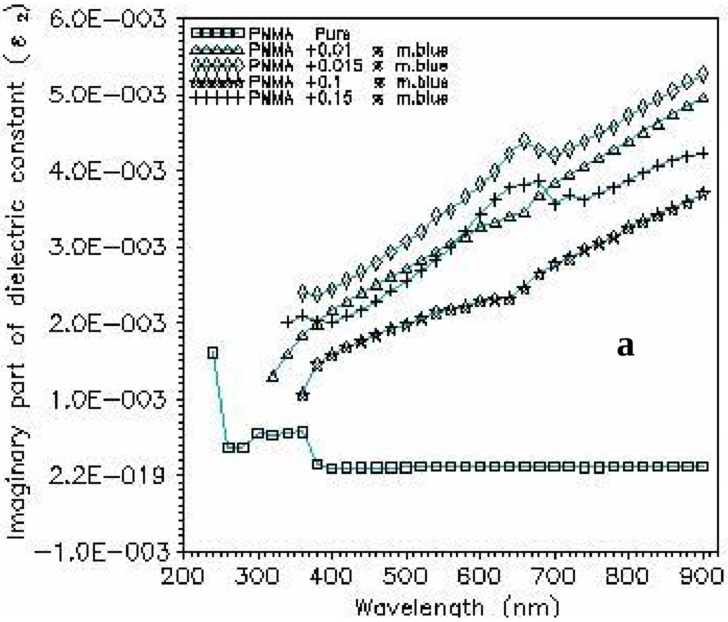


Fig.(3)Variation in real part of dielectric constant (ε_1) as function of wavelength of pure and doped PMMA with: (a) mb with different concentrations,(b)mr with different concentrations.



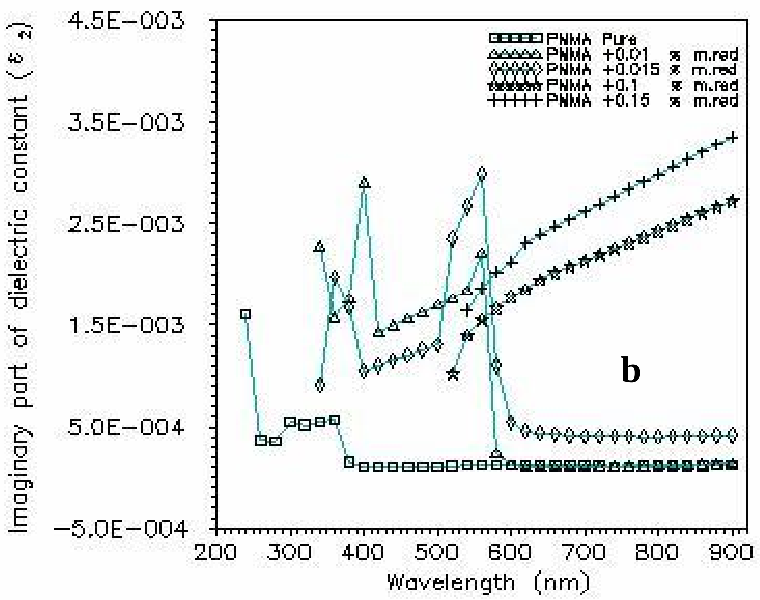


Fig.(4)Variation in imaginary part of dielectric constant (ε_2) as function of wavelength of pure and doped PMMA with: (a) mb with different concentrations,(b)mr with different concentratio