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Nonlinear Optical Properties of PMMA Composites Using Z-Scan Technique

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Abstract: The nonlinear refractive index and the nonlinear absorption coefficient of unmodified and functional poly(methyl methacrylate) PMMA films were studied before and after the addition of the filler by the z-scan technique, using a Q-switched Nd:YAG laser at two wavelengths: 532 nm and 1064 nm, and at three input energies (13, 33 and 53) mJ. Both linear and nonlinear refractive indices and absorption coefficients of polymer films were studied by using UV-VIS spectrophotometer. The results show that the creation of functional PMMA from unmodified PMMA will increase the nonlinear optical properties in the functional PMMA/copper matrix more than in the unmodified PMMA/copper matrix. Hence, the functional PMMA appears promising as a useful third-order nonlinear material. The nonlinear refractive index is directly proportional to the input intensity and directly proportional to the increase in the concentration of the filler, while the nonlinear absorption coefficient is inversely proportional to the input energy and inversely proportional to the increase in the concentration of the filler. The nonlinear effect is more enhanced at the 532 nm wavelength than at 1064 nm..

Introduction

There is considerable interest in finding materials having large yet fast nonlinearities. This interest, which is driven primarily by the search for materials for all-optical switching and sensor protection applications, concerns both nonlinear absorption (NLA) and nonlinear refraction (NLR). [1]. Amongst the nonlinear materials, organic polymers are particularly attractive because of its properties such as low density, mechanical flexibility and a high nonlinear response [2]. During the recent years, nonlinear optical properties have been the subject of numerous investigations theoretically and experimentally due to their applications [3]. Furlani et al. used symmetric and non-symmetrical Pt (II) and Pd (II) bis-acetylides complexes and those dispersed in PMMA. Their nonlinear optical properties were measured using the z-scan technique with mode locked Ti-sapphire delivering pulse width of 150 fs with a wavelength of 770 nm [4]. Lee et al. reported the fabrication of gold-PMMA stacks and their linear and nonlinear optical properties [5]. Shettigar et al. studied the nonlinear optical parameters of bis_cholcone derivatives doped in PMMA matrix in a z-scan technique, by using 7ns Nd:YAG laser pulses at 532nm wavelength[6]. Mathews et al. studied the nonlinear optical and optical limiting properties of tetra tert-butyl phthalocyanine and zinc tetra tert-butyl phthalocyanine at 633 nm wavelength using a continuous wave laser[7]. Shettigar et al. have investigated third-order nonlinear optical properties 3-phenyl sydones doped into PMMA and determined both real and

imaginary parts of the third order nonlinear succeptibility, $\chi 3$ [2].

The z-scan technique is a relatively simple and direct method to characterize both the nonlinear refraction index and nonlinear absorption coefficient [8]. It is based on the nonlinear transverse modification of the laser beam throughout its focal length resulting in the intensity variation experienced by a sample which is moved along the propagation axis of the laser beam (z-axis) near the focal position [9]. When a small aperture is placed in front of the detector, it provides a measurement for the refractive index nonlinearity, while open aperture z-scan experiments are sensitive to the intensity dependent absorption coefficient [1]. The set-up of the z-scan system is shown in Figure 1

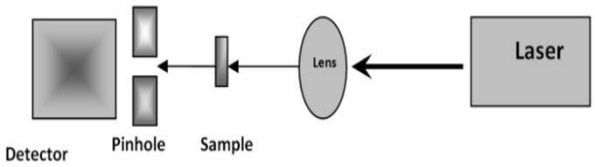

Fig (1): The setup of the z-scan system

The experiment

The poly (methyl methacrylate) PMMA supplied by BDH Chemicals LTD ,England, with 99.8% purity, is used. The kind of filler used in this work, which is a copper ion source, was created from CuCl2.2H2O powder (from BDH Chemicals LTD, England), with 99.8% purity. Acetone was used as a solvent for PMMA, supplied by (BDH chemicals LTD England), with 99.9% purity. The unmodified PMMA was created by dissolving 0.7 g of PMMA in 10 ml acetone to get the homogenous solution. The magnetic heater stirrer was used as a source of heating and to mix the solution. The degree of heat must be less than the degree of its glass transition temperature (Tg=105 □C). The functional PMMA were synthesized from unmodified PMMA by the base hydrolysis of the methacrylate groups in unmodified PMMA to forming carboxylate groups in functional PMMA. This process is shown in the equation:

$$(-CH_2-C(CH_3)COOCH_3)_{-n} + mOH$$

$$= (-CH_2-C(CH_3)COOCH_3)_{-nm}(-CH_2-C(CH_3)COO^-)$$

$$(1)_{-m} + mCH_3OH$$

Where m,n are a number of moles.

A copper ion was created by dissolving different weights of CuCl2.2H2O (0.02, 0.04, 0.06, 0.1 and 0.14 g) in 10 ml of acetone and stirred in magnetic stirrer without heating for 1 hour [5]. After preparing unmodified PMMA, the solution of CuCl2.2H2O in acetone was added, then mixed using magnetic stirrer with heating the solution for 3 hours in order to avoid molecular aggregation. To get functional PMMA-CuCl2.2H2O: the CuCl2.2H2O in acetone was added to functional PMMA, which is prepared as mentioned before, by using the magnetic stirrer. The unmodified PMMA, functional PMMA and composite polymer solutions are pouring in a glass plate (2x7x5cm). To remove possible residual solvent, film samples were further dried at room temperature overnight .

The atomic absorption/flame emission spectrophotometer (Shimadzu A.A 160 A) was used to calculate the amount of metal absorbed by the polymer and expressed in terms of mill equivalent per gram of polymer (m.eq.g -1.(

Optical techniques are used for measuring (linear and nonlinear properties) linear optical testing and nonlinear measurement. The Michelsons interferometer was used to measure the thickness of the samples' film . It was found to be equal to (5.3) μm. The thickness of the film equals 5.3 μm.

Z-Scan measurements were performed in two parts, closed and open aperture. The closed-aperture was used to measure the nonlinear refractive index, while the open-aperture was used to measure the nonlinear absorption coefficient. Each part was carried out withNd:YAG at 1064 nm and 532 nm using KTP crystal. [4,13,14].

Results and Discussion

In the atomic absorption/flame emission spectrophotometer, the amount of Cu+2 from CuCl2.2H2O in unmodified PMMA and functional PMMA was measured. It was found to be equal to 0.58 (m.eq.g-1) in unmodified PMMA and 1.262 (m.eq.g -1) in functional PMMA. Results showed that the capacity of functionalized PMMA for Cu+2 is larger than in unmodified PMMA. This indicates the ability to bind Cu+2 ions. The ability is enhanced by base-catalyzed hydrolyses of methacrylate groups in unmodified PMMA to format

carboxylate groups. This is likely to increase the likelihood of precipitating inorganic particles within the polymer matrix [15].
UV-VIS absorption spectrum was obtained for unmodified PMM after the addition of filler as shown in Figure 2.

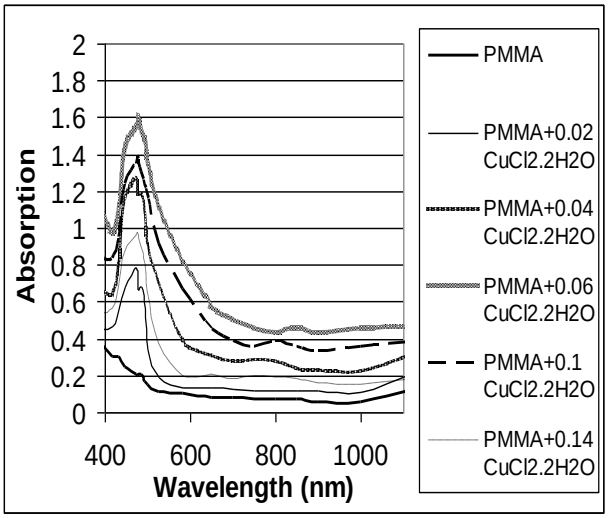

Fig. (2): UV-VIS absorption spectra of unmodified PMMA after adding the filler

The peak at 476 nm seems to correspond to the PMMA copper association. It is corresponding to a shift in the d-d transition of the copper due to the binding with polymer [15.[
UV-VIS absorption spectrum for functional PMMA after the addition of filler is shown in Figure 3.

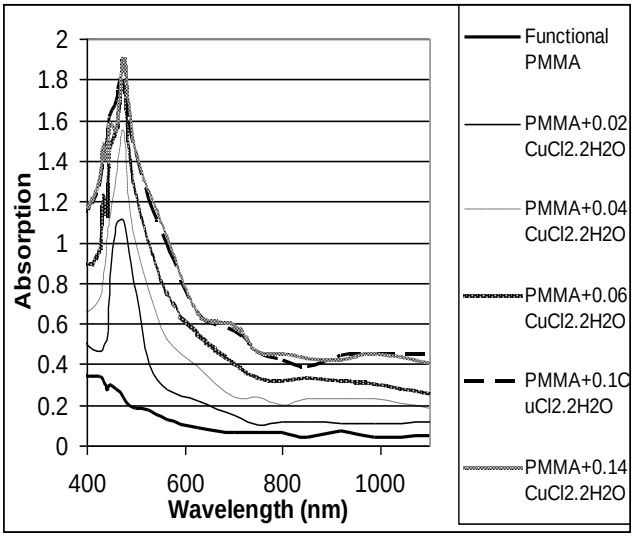

Fig. (3): The UV-VIS absorption spectra of functional PMMA after adding the filler

The intensity of functional PMMA spectra is higher than the intensity of the unmodified polymer spectra. The intensity of the peak is larger than the peak in unmodified polymer. The same behavior can be seen for the peak position in functional PMMA, which means copper association. When CuCl2.2H2O is added, the peak at 476 nm seems to correspond to the PMMA copper association. Figure 4 represents a comparison in the absorbance at 476 nm as a function of copper concentration in both unmodified PMMA and functional PMMA. Figure 4 represents a comparison in the absorbance at 476 nm as a function of copper concentration in both unmodified PMMA and functional PMMA.

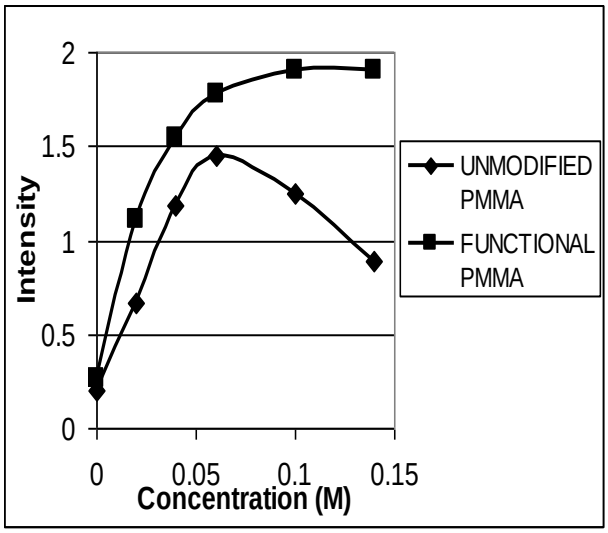

Fig. (4): The absorbance at 476 nm as a function of copper concentration in both unmodified PMMA and functional PMMA

It can be seen from Figure 4 that the absorbance for both polymers initially increases linearly with increasing copper concentration. It reaches a plateau, corresponding to reaching the binding capacity of the polymer for Cu+2 ions. The capacity of the functionalized polymer for Cu+2 is greater than unmodified PMMA. This indicates that the ability to bind Cu+2 ions is enhanced by base-catalyzed hydrolysis of the ester groups to carboxylate groups. This behavior of absorption curves is in good agreement with the result reported by Lubeck [16].The nonlinear refractive index for unmodified and functional was measured. Figure 5 shows the closed-aperture z-scan of unmodified PMMA at 1064 nm and 532 nm for 13 mJ, 33 mJ and 53 mJ

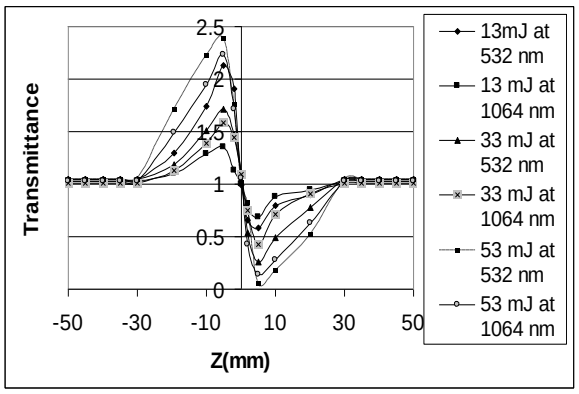

Fig. (5): The closed-aperture Z-scan of unmodified PMMA

The same behavior appears in functional PMMA, 0.02 M CuCl2.2H2O in unmodified PMMA and 0.02 M CuCl2.2H2O in functional PMMA. (The same phenomenon appeared with functional PMMA in all the closed-aperture curves). In this mechanism, the maximum and minimum transmittance occurred at z equal to (5) mm and (-5) mm respectively. A peak followed by a valley at 1064 nm and at 532 nm is the hallmark of a negative n2.The peak to valley profile, displayed in the figures, demonstrates that the sample exhibited a self-defocusing effect. The nonlinear refractive index of unmodified PMMA, functional PMMA, 0.02M CuCl2.2H2O in unmodified PMMA and 0.02M CuCl2.2H¬2O in functional PMMA have been calculated from the variable transmittance values at two wavelengths, 532 nm and 1064 nm. The nonlinear refractive index depends on the energy and the wavelength of the laser. The behavior of n2 to the input fluence for unmodified and functional PMMA at different energies at 532 nm and 1064 nm can be shown in Figure 6, while the behavior of n2 to the input fluence for 0.02M CuCl2.2H2O unmodified and functional PMMA at different energies at 532nm and 1064 nm can be shown in Figure 7.

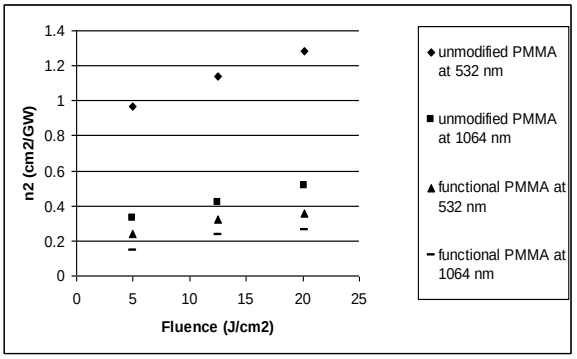

Fig. (6): The behavior of n_2 to the input fluence for unmodified and functional PMMA

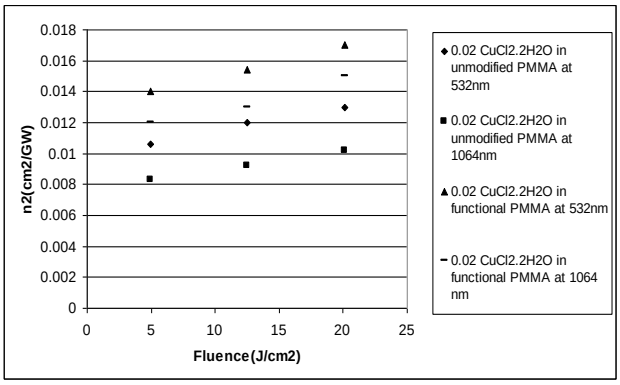

Fig. (7): The behavior of n_2 to the input fluence for $CuCl_2.2H_2O$ in unmodified and functional PMMA at 0.02 M concentration of PMMA $CuCl_2.2H_2O$

The nonlinear refractive index of the polymer thin films was affected by the addition of NaOH and different concentrations of filler. Figure 8 shows closed aperture measurement of unmodified and functional PMMA with different concentration of CuCl2.2H2O at 532nm at 13 mJ, while Figure 9 shows closed aperture measurement of unmodified and functional PMMA with different concentrations of CuCl2.2H2O at 1064 nm at 13 mJ.

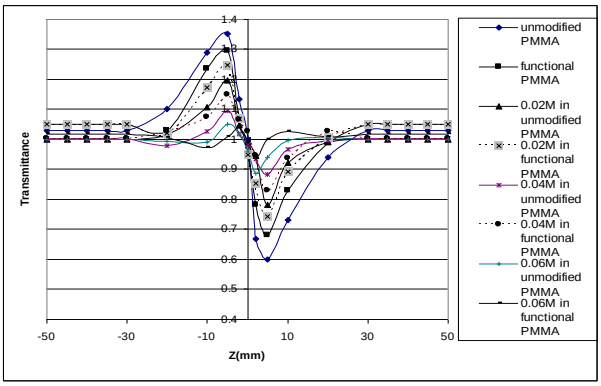

Fig. (8): unmodified and functional PMMA with different concentrations of $CuCl_2.2H_2O$ at 13 mJ at 1064nm

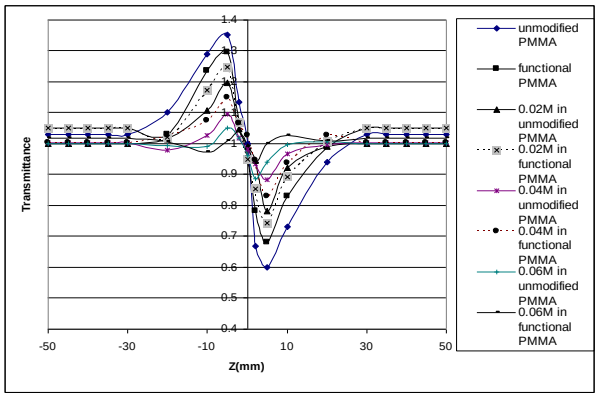

Fig. (9): unmodified and functional PMMA with different concentrations of CuCl2.2H2O at 13 mJ at 1064nm

Figure 10 represents the relation between nonlinear refractive index and the concentration of the filler at 532nm, and Figure 11 shows the relation between nonlinear refractive index and the concentration of the filler at 1064nm as shown below.

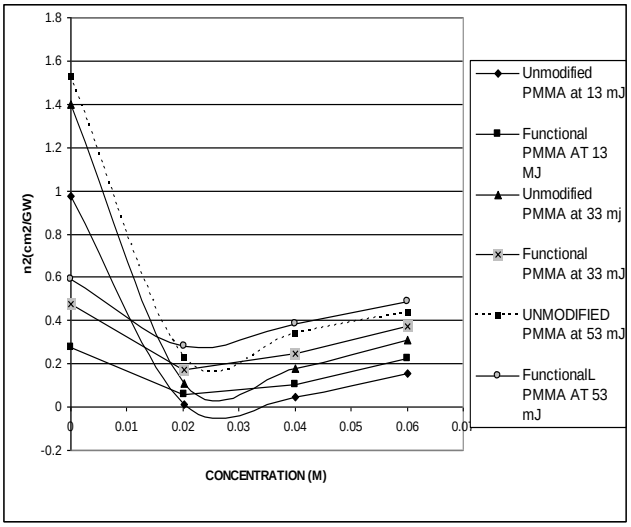

Fig. (10): represents the relation between n_2 and different concentrations in both unmodified PMMA and functional PMMA at 532nm

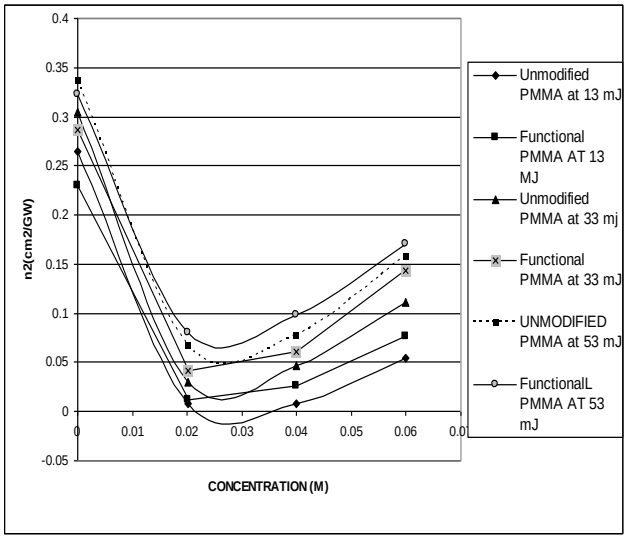

Fig. (11): shows the relation between n_2 and different concentrations in both unmodified PMMA and functional PMMA at 1064nm

The refractive index in functional PMMA is smaller than in unmodified PMMA in both wavelengths of 532 nm and 1064nm. The addition of NaOH to unmodified PMMA caused a change in the refractive index. So the presence of overlapping between regions of different refractive indices will cause will cause scattering of the light and increasing absorbance of the light by the new functional group. The refractive index will be less than in unmodified PMMA [17]. The same behavior can be seen in the wavelengths 532 nm and 1064 nm. Adding CuCl2.2H2O to both unmodified and functional PMMA, the magnitude of n2 is larger than when adding the filler to the polymer thin films. The result is due to the CuCl2.2H2O. This material absorbs visible light [18]. All these reasons will cause the refractive index to decrease with the addition of CuCl2.2H2O to the unmodified PMMA and functional PMMA [18].

The magnitude n2 started with a small increase at low concentration. At a higher concentration, the value of n2 increased very strongly in both functional and unmodified PMMA when adding CuCl2.2H2O at (532) nm and (1064) nm. In functional PMMA-CuCl2.2H2O, the magnitude of n2 is larger than in unmodified PMMA-CuCl2.2H2O at the same concentration of CuCl2.2H2O, with the same wavelength and at the same energy, because the capacity of the functionalized polymer for Cu+2 is greater than unmodified PMMA. The magnitude of n2 is increased with the increasing of the concentration of CuCl2.2H2O for the two polymers (functional and unmodified PMMA.(

The effect of nonlinear absorption in unmodified PMMA is shown in Figure 12 at different energies. In functional PMMA, the behavior of transmittance as a function of sample position a long z-scan can be investigated from Figure 13 at different energies

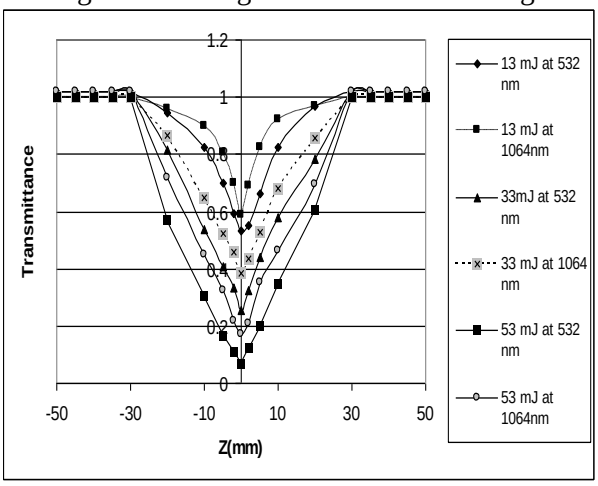

Fig. (12): The open-aperture Z-scan of unmodified PMMA

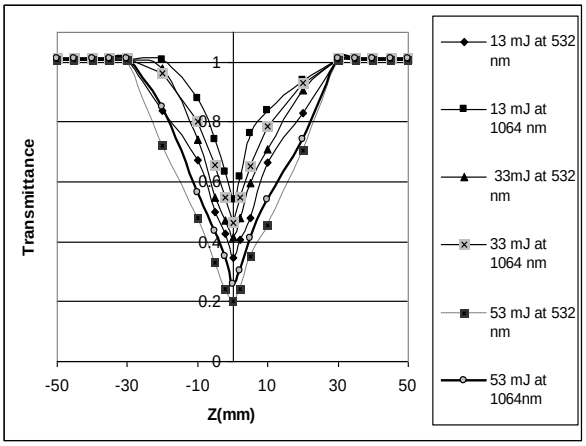

Fig. (13): The open-aperture z-scan of functional PMMA

Figure 14 and Figure 15 represents the open aperture for unmodified and functional PMMA with 0.02M concentration of CuCl2.2H2O

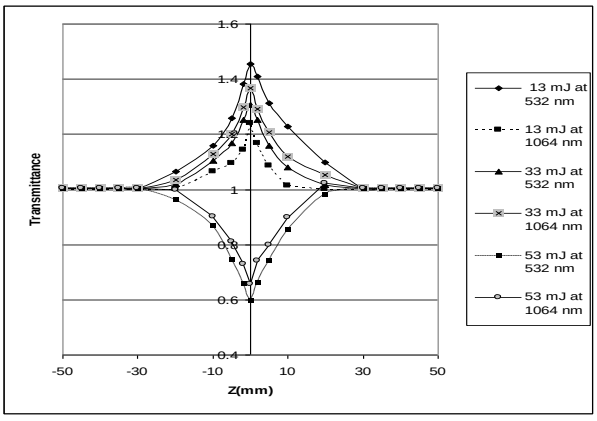

Fig. (14): The open-aperture Z-scan of 0.02M $CuCl_2.2H_2O$ in unmodified PMMA

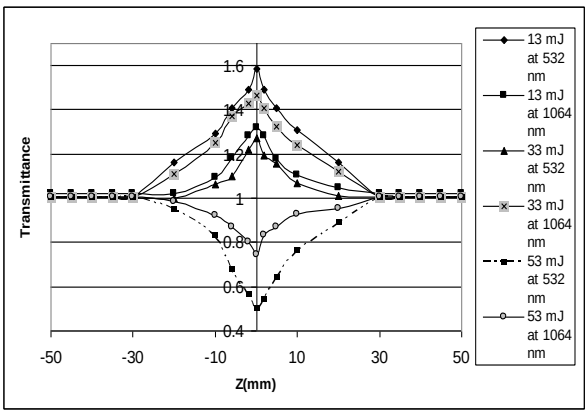

Fig. (15): The open-aperture Z-scan of 0.02M $CuCl_2.2H_2O$ in functional PMMA

The transmittance is sensitive to the nonlinear absorption as a function of input energy pulses. In unmodified PMMA and functional PMMA, the change in intensity is caused by two-photon absorption. In unmodified PMMA and functional PMMA with CuCl2.2H2O at 13 mJ and 33mJ, the change in intensity is caused by saturable absorption. Increasing energy to 53mJ, the sample starts showing two-photon absorption.The behavior of β to the input fluence for unmodified and functional PMMA at different energies, at 532nm and 1064 nm can be shown in Figure 16, but Figure 17 shows the behavior of β to the input fluence for 0.02M CuCl2.2H2O in unmodified and functional PMMA at different energies, at 532nm and 1064 nm

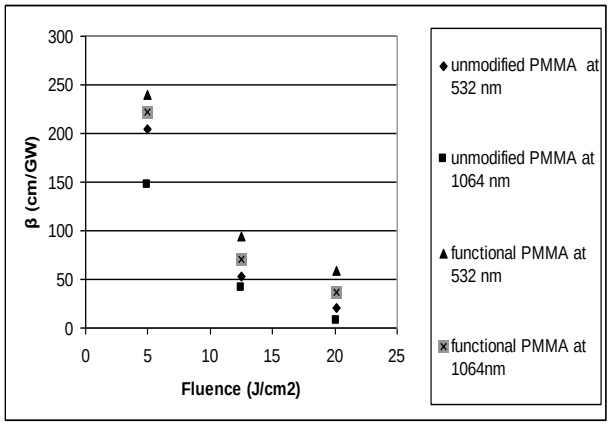

Fig. (16): the relation between fluence and β in functional and unmodified PMMA

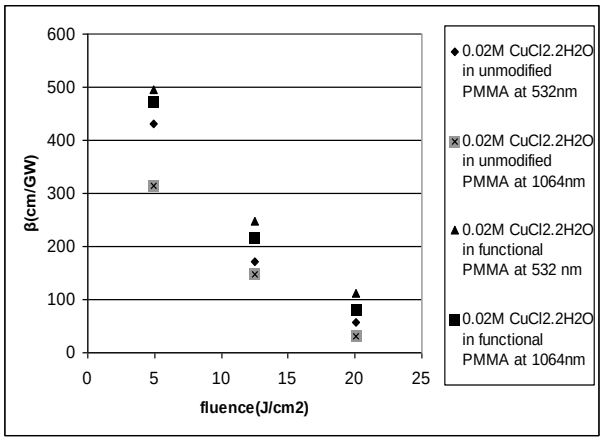

Fig. (17): the relation between fluence and β in functional and unmodified PMMA with 0.02M $CuCl_2.2H_2O$

At 1064 nm, the magnitude of β is independent of the intensity. This property is more enhanced at 532 nm, so the magnitude of β at 532nm is larger than at 1064nm, which means that the nonlinear effect is increased at the focal point at wavelength 532nm more than in 1064nm. The magnitude of β is decreased with the increase in fluence, which means the nonlinear absorption

coefficient β is inversely proportional to the input energy.

The nonlinear absorption coefficient of the polymer thin films was affected by the addition of NaOH and different concentration of filler. Figure 18 shows the behavior of open aperture of unmodified and PMMA with different concentrations of CuCl2.2H2O at 532nm and 13 mJ.

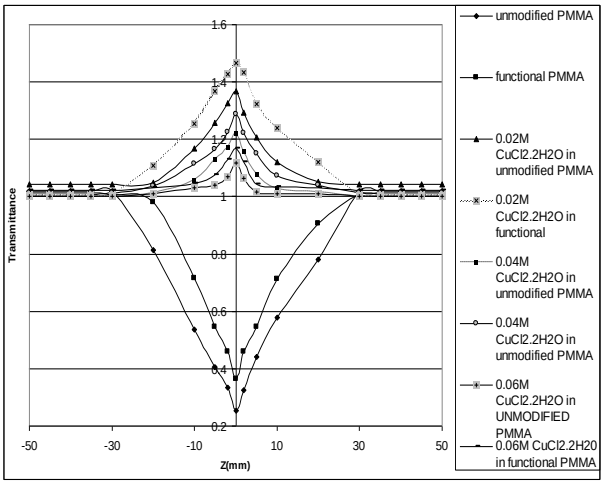

Fig. (18): open aperture of unmodified and functional PMMA at 532 nm and 13mJ

The same behavior was obtained for open aperture at 33mJ and at 532 nm. Open aperture at 532 nm and at 53 mJ of unmodified and functional PMMA with different concentration of CuCl2.2H2O can be investigated in Figure 19.

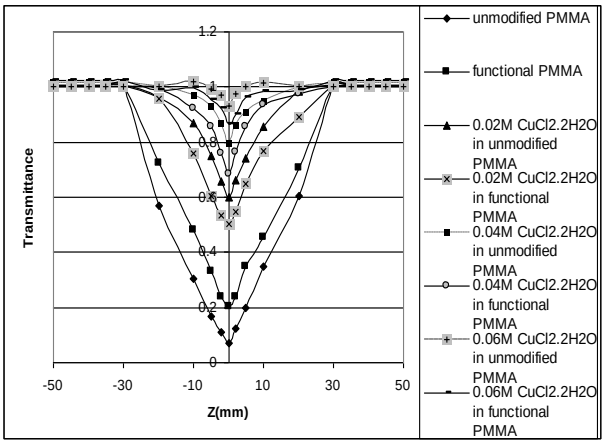

Fig. (19): open aperture of unmodified and functional PMMA at 532 nm and 53mJ

At 1064nm, the behavior of open aperture of unmodified and functional PMMA with different concentrations of CuCl2.2H2O at 13 mJ is represented in Figure 20.

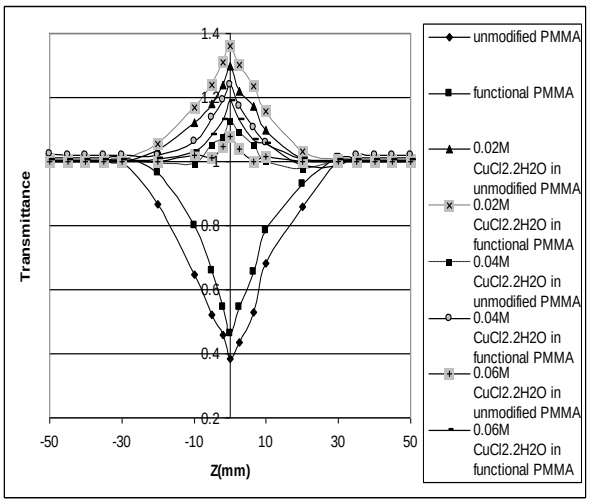

Fig. (20): open aperture of unmodified and functional PMMA at 1064 nm and 13mJ

The same behavior of open aperture appeared at 33mJ and at 532 nm. Figure21 summarizes the behavior of open aperture of unmodified and functional PMMA with different concentrations of CuCl2.2H2O at 1064nm and 53 mJ.

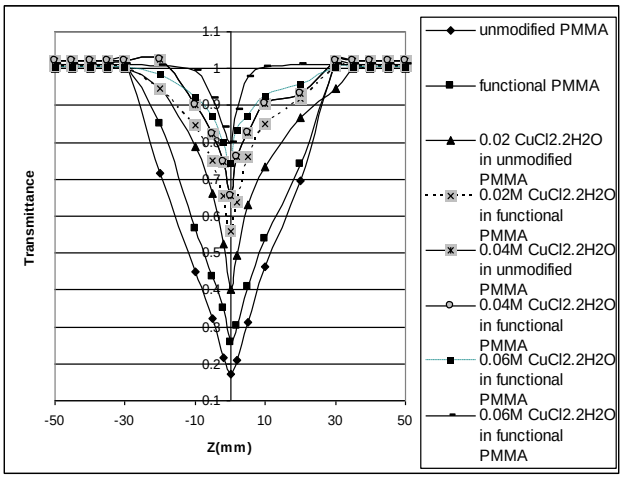

Fig. (21): open aperture of unmodified and functional PMMA at 1064 nm and 53mJ

Figure 22 summarizes the relation between β and different concentrations in both unmodified PMMA and functional PMMA when adding different concentrations of CuCl2.2H2O at 532 nm, while the relation between β and different concentrations in both unmodified PMMA and functional PMMA when adding different concentrations of CuCl2.2H2O at 1064 nm is shown in Figure 23.

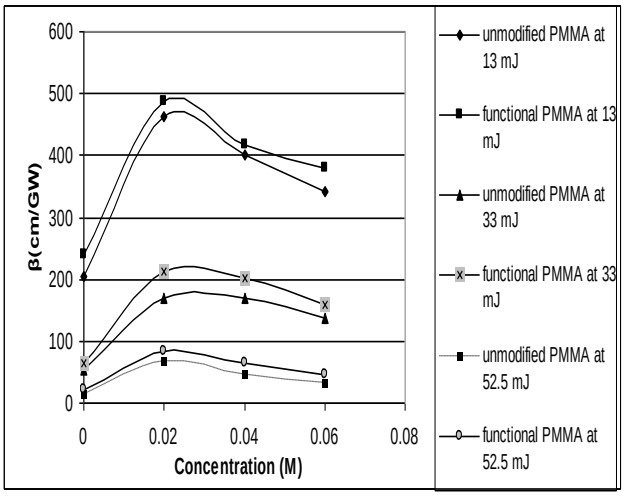

Fig. (22): The relation between the concentration of $CuCl_2.2H_2O$ and β at 532 nm

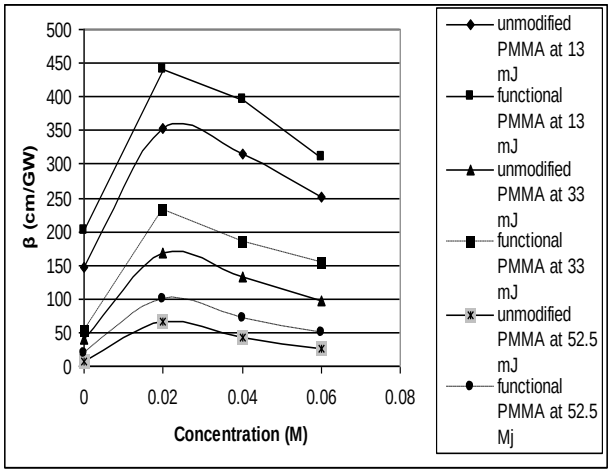

Fig. (23): The relation between the concentration of $CuCl_2.2H_2O$ and β at 1064 nm

The absorption coefficient in functional PMMA is higher than in unmodified PMMA for both wavelengths, at 532 nm and 1064nm. The magnitude β is inversely proportional to the concentration of the filler in both functional and unmodified PMMA. In functional PMMA-CuCl2.2H2O, the magnitude of β is larger than in unmodified PMMA- CuCl2.2H2O at the same concentration of CuCl2.2H2O, at the same wavelength and at the same energy, because the capacity of the functionalized polymer for Cu+2 is greater than unmodified PMMA. Before adding CuCl2.2H2O to both unmodified and functional PMMA, the magnitude of β is smaller than after adding the filler to the polymer thin films.

Conclusions

The capacity of functionalized PMMA for Cu+2 is greater than unmodified PMMA, and the creation of functional PMMA from unmodified PMMA will increase the nonlinear optical properties in functional PMMA/copper matrix more than in unmodified PMMA/copper matrix. Hence, the functional PMMA appears promising as a useful third-order nonlinear material. The nonlinear refractive index is directly proportional to the input intensity and directly proportional to the increase in the concentration of the filler. While the nonlinear absorption coefficient is inversely proportional to the input energy and inversely proportional to the increase in the concentration of the filler. The nonlinear absorption coefficient in unmodified PMMA and functional PMMA is caused by the effect of two photon absorption. When the copper (II) chloride dehydrate is added to the polymer matrix, the nonlinear absorption coefficient at the low intensity is caused by the saturable absorption, while at high intensity it is caused by two photon absorption. The nonlinear effect is more enhanced at the wavelength 532 nm than at 1064 nm.

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دراسة الصفات البصرية اللاخطية لمتراكبات البولي مثيل ميثا اكريلت بأستخدام تقنية المسح على المحور الثالث

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الخلاصة : تم دراسة معامل الانكسار اللاخطي ومعامل الامتصاص اللاخطي لأغشية البولي مثيل ميثا اكريلت المحور وقبل التحوير بأضافة ماليء بأستخدام تقنية المسح على المحور الثالث بأستخدام ليزر النديميوم –ياك النبضي عند طولين موجيين 1064 و532 نانومتر. ولثلاث طاقات ليزرية 13, 33, و53 ملي جول. وكذلك تم ايجاد معامل الانكسار ومعامل الامتصاص الخطي بأستخدام جهاز المطياف. النتائج اظهرت ان البوليمر المحور والمكون بأضافة ماليء تزداد فيه االصفات البصرية اللاخطية ظهورا مع زيادة نسبة الماليء وهو النحاس. وبذلك فأن المتراكب الفعال اظهر امكانية استخدامه كمادة لاخطية . ووجد ايضا أن معامل الانكسار اللاخطي يتناسب طرديا مع الشدة الليزرية ومع الزيادة في تركيز الماليء ,بينما بالنسبة لمعامل الامتصاص اللاخطي فأنه يتناسب عكسيا مع الزيادة في تركيز الماليء . التأثير اللاخطي يزداد عند الطول الموجي 532 نانومتر اكثر منه عند الطول الموجي 1064 نانومتر.