Iraqi J. Laser, Part A, Vol. 10, pp. 23-29 (2011)

IRAQI JOURNAL OF LASER

The Optical Limiting Behaviour of Prepared Silver Nanoparticles Embedded in Polymer Film

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(Received 3 November 2011; accepted 1 April 2012)

Abstract: In the present work, silver nanoparticles were prepared. Nonlinear optical properties and optical limiting of silver nanoparticles were investigated.Standard chemical synthesis method was used at diffrent weight ratio(0.038, 0.058 and 0.078) of silver nitrate. Several testing were done to obtain the characteristics of the sample. Z-Scan experiments were performed using 30 ns Q-switched Nd:YAG laser at 1064 nm and 532 nm at different intensities. The results showed that the nonlinear refractive index is directly proportional to the input intensities, which caused by the self-focusing of the material. In addition, the optical limiting behavior has been studied. The results showed that the sample could be used as an optical limiter device for a wide range of the input energies.

Introduction

Nanostructure materials are anew type of materials that exhibit unique features and properties in different fields [1]. Synthesis of nanoparticles in matrixes such as polymer films are of major interest in several optical, nonlinear optical, and sensor applications [2]. Nonlinear optical thin films are developed and studied for future photonic application due to their high nonlinearity, fast response time and good compatibility with fabrication of wave guide and intergraded optical devices. One of the possible approaches is utilizing third order nonlinear optical properties of such materials. In particular , the ability of these materials to change the value of refractive index under the action of applied optical field [3].One of these materials is silver nanostructure because of silver nanoparticles interact with light are stronger than any known chromophore [4]. Z-scan is a simple and an accurate method to study the nonlinear properties .This technique can be used to obtain the nonlinear absorption coefficient and sign and magnitude of nonlinear refractive index (n2) by observing the self-focusing or self-defocusing of a tightly focused laser beam as the sample is scanned through the focal region [5].The Z-scan method provides a sensitive and a straightforward method for the determination of the nonlinear refractive index and the nonlinear absorption coefficient. The technique has been widely employed for characterizing the optical nonlinearity of nanomaterials[6]. The relative on-axis transmittance of the sample measured (at the small aperture of the far-field detector) for measuring n2 is given by [7]:-

$$T(z,\Delta\Phi o) = 1 - \frac{4\Delta\Phi o\, Z/Zo}{[(Z^2/Zo^2)+9][(Z^2/Zo^2)+1]} \quad (1)$$

Where T is the transmittance through the aperture, which is a function of the sample position Z, the nonlinear refractive index is calculated from the peak to valley difference of the normalized transmittance by the following formula [8] :-

$$n2 = \Delta\Phi o / Io\ Leff\ k \qquad (2)$$

where, k = 2π /λ , λ ,is the wavelength of the beam. Leff :- the effective length of the sample and ΔΦo :- nonlinear phase shift which is equal to

$|\Delta\Phi o| = \Delta Tpv / 0.406(1\text{-}S)0.27$ S is the fraction of beam transmitted through the aperture, and $S = 1 - \exp(-2\ ro2 / wo2)$, ro and wo being the aperture and the beam radii respectively.

The normalized change in transmitted intensity can be approximated by the following equation[9] :

$$T(z) = \sum_{m=0}^{\infty} \frac{\left[\dfrac{\beta I_o L_{eff}}{1+(Z/Zo)^2}\right]^m}{(m+1)^{3/2}} \qquad (3)$$

Where:

Z: - is the sample position at the minimum transmittance, *m* :- integer number.

T(z):- the minimum transmittance. The two terms in the summation are generally sufficient to determine ***β*** [9].

Silver nanoparticles in polymer appear to be attractive candidates for optical limiting application and sensor applications.

An ideal optical limiter is one which is perfectly transparent at low intensities up to a predetermined intensity level, above which the transmitted intensity remains clamped at a constant value [6].

Experimental Details

Silver nanopartices in PVA (poly vinyl alcohol) was formed by spin cast the mixture of PVA and AgNO3 .Silver nanoparticles were formed by the standard chemical method which include the reduction of silver ions using PVA as a reducing agent. A silver nanoparticles were created by dissolving different weights of AgNO3 (0.038,0.058, and 0.078gm) in 5 ml of warm deionized distalled water then adding 1 gm of PVA in water bath around (90^oC) for 3 hours after that the homogeneous solution coated by spin coating instrument over the PS(poly styrene) films by adding 0.5ml of this solution over the slide for 5 sec in 100 rpm, and then leave it to dry for 1 hour at room temperature.

The atomic absorption / flame emission spectrophotometer were used to calculate the amount of metal absorbed by the polymer and expressed in terms of milli equivalent per gram of polymer (m.eq.g-1). A PW 1840 diffractometer equipped with a radiation source (40 KV, 20 mA) and λ = 0.154 nm was used to extracted x- ray spectrum. The sample was scanned in the range from (10o to 90o).

Finally the nonlinear optical properties of the sample were extracted using Z-scan technique. Closed aperture Z-scan for nonlinear refractive index by using aperture and open aperture Z-scan for nonlinear absorbtion cofficient .Q-switch Nd:YAG laser at 1064 nm and 532 nm was used.The set-up is shown in Fig. (1). Photo-detector *PD* collects the light that passes through an axially centered aperture *A* in the far field and the sample *S* travels through the beam waist [5].

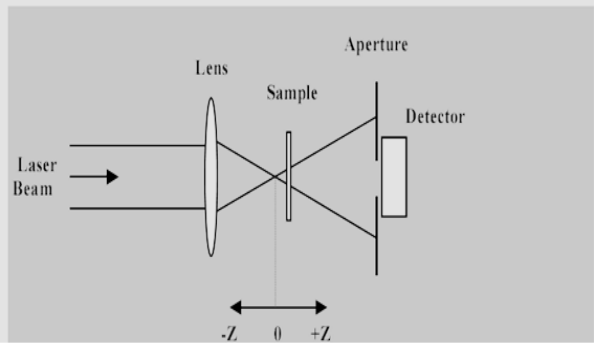

Fig. (1): Experimental set-up of Z-Scan system.

Results and Discussion

Silver Nanoparticles Properties

In Atomic Absorption/Flame Emission Spectrophotometer technique, the amount of Ag in polymer was measured. It was found equal to (1.63 ,2.64,4.56) (m.eq.g -1) respectively. This is likely to increase the likelihood of precipitating inorganic particles within the polymer.

The X-Ray diffraction pattern of Silver nanoparticles is shown in Figure 2. XRD of the silver nanoparticles reveals diffraction peaks corresponding to the cubic structure form. The data shows diffraction peaks at 2θ = 38.2°, 44.4°, 64.6°, 77.5°, and 81.7°, which can be indexed to (111), (200),(220), (311), and (222) planes of pure silver respectively. According to Scherer formula the average sizes of the nanoparticles are 13 nm. This calculation shows the Ag particles are nanoparticles.

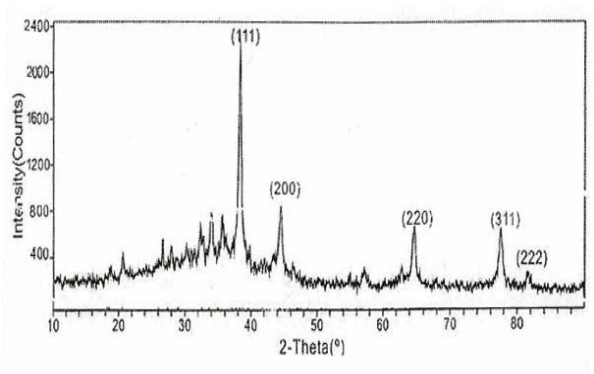

Fig. (2):X-ray diffraction pattern of multi layer polymers with 0.058gm filler.

In order to investigate the nonlinear refractive index, there are two cases were chosen at 1064 nm and at 532 nm. Figures (3), (4), (5) show the closed-aperture Z-scan results at (1064, 532) nm at different intensities each case with three weight ratio of filler.

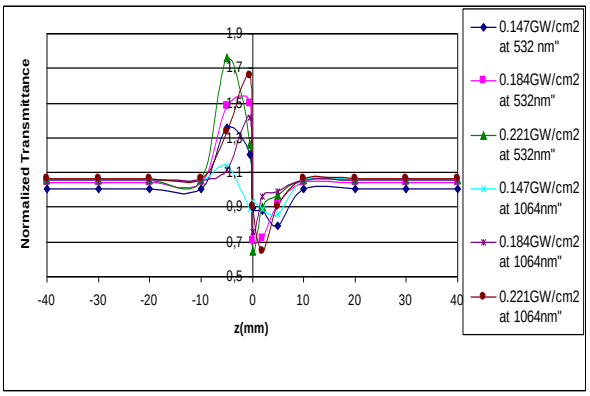

Fig. (3): Closed-aperture Z-Scan for 0.038 weight ratio of composite

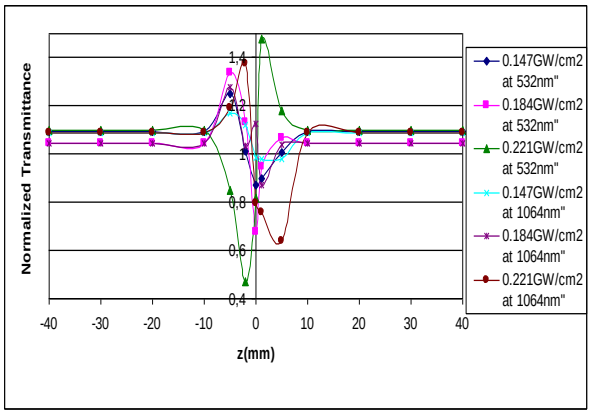

Fig. (4): Closed-aperture Z-Scan for 0.058 weight ratio of composite.

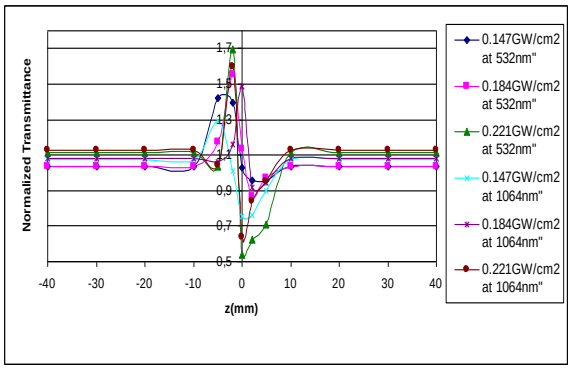

Fig. (5): Closed-aperture Z-Scan for 0.078 weight ratio of composite

The transmittance started with a linear behavior at different distances from the far field of the sample position (-Z) with respect to the focal plane at Z=0 mm. The change in on-axis intensity is caused by self-focus or self-defocus by the sample as it travels through the beam waist [12,13]. This modified refractive index distribution then acts like a focusing lens.
A valley followed by a peak is the hallmark of a positive *n2* i.e., it has a positive nonlinearity at 1064 nm and at 532 nm. The external self-focusing arising from the Kerr effect in silver nanoparticles, which appears in the peak and valley transmittance of each of Z-scan trace. The same behavior can be seen at the wavelength 532 nm and 1064 nm. A negative z-scan profile can be shown for all the Figures, the only difference can be shown in 0.058 weight ratio of filler composite which shown a positive z-scan profile at 0.221 GW/cm2 at 532 nm .The magnitude of n2 is increased with the increasing of the weight ratio of the filler for the two wavelength, unless at 0.058 weight ratio of filler. Thermal effects in organic materials generally give rise to negative n2 with increasing the weight ratio of filler [14]. The closed-aperture Z-scan defines variable transmittance values, which used to determine the nonlinear phase shift $\Delta\Phi$ and the nonlinear refractive index using Eq. (2). The magnitude of *n2*, at higher intensities the value of *n2* increased strongly. The same behavior can be observed at 532 nm. The results show different values of *n2*, which is calculated using Eq. (2), and $\Delta\Phi$, which correspond to the change in the input intensity, direction and the wavelengths used. As a comparison to the input intensity, the value of *n2* is increased as the intensity increased. This behavior is more enhanced at 532 nm than for 1064 nm as shown in Figures (6, 7, 8, 9).

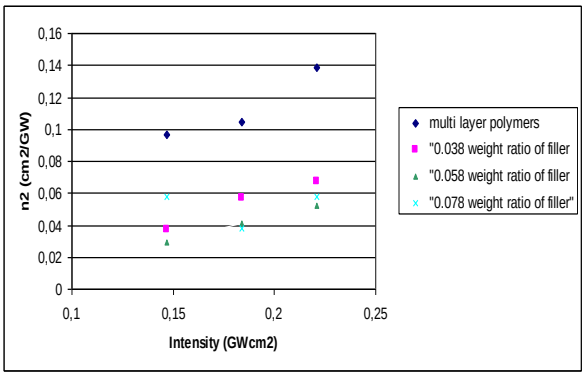

Fig (6): The relation between n2 and intensities for different weight ratio of filler at 532 nm

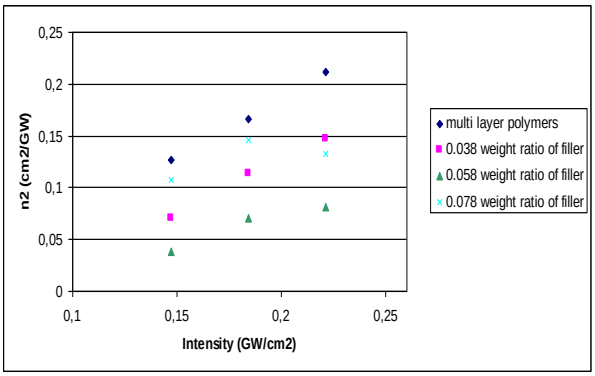

Fig. (7): The relation between n2 and intensities for different weight ratio of filler at 1064 nm

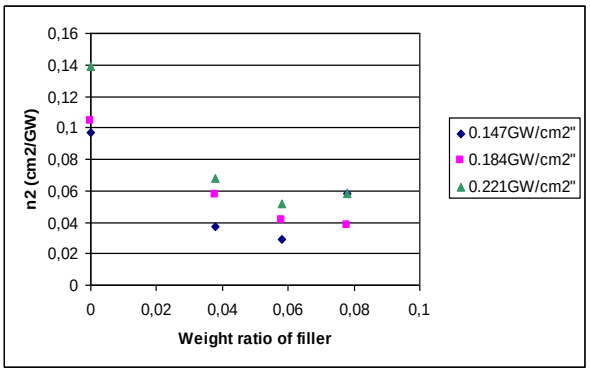

Fig. (8): The relation between n2 and different weight ratio of filler at 532nm

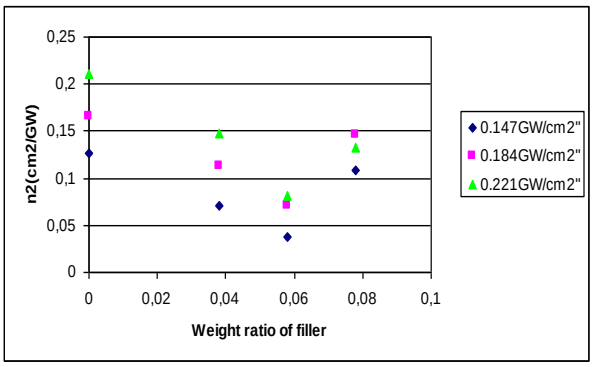

Fig. (9): The relation between n2 and different weight ratio of filler at 1064 nm

This was attributed to the higher intensity, which leads to the higher nonlinear effect especially at near the focal plane. This variation may arise from such contributions as self-focusing of a sample The nature of the nonlinear response can be inferred from its dependence on intensity. Since, the silver nanoparticles film exhibit a third order (Kerr) nonlinearity over the intensity range measured, the values of *n2* for as a function of intensity implies a dependence of the nonlinear refractive index on the input intensity.Figures (8,9) represent the relation between nonlinear refractive index and the weight ratio of the filler at 532nm and1064nm. The magnitude of n2 is increased with the increasing of the weight ratio of the filler for the two wavelength, unless at 0.058 weight ratio of filler. Thermal effects in organic materials generally give rise to negative n2 with increasing the weight ratio of filler [14]. The open-aperture Z-scan defines variable transmittance values, which used to determine the nonlinear absorption coefficient using Eq.(3). In order to investigate the nonlinear absorption coefficient, there are two cases were chosen at 1064 nm and at 532 nm. Figures (10), (11), (12) show the open-aperture Z-scan results at (1064, 532) nm at different intensities of the laser source each case with three different weight ratio.

The change of the intensity in the Figures (10), (12), and 0.038 and 0.078 weight ratio of filler in Figure (11) are caused by two photon absorption in the sample travels through beam waist. The observed results are explained through an energy transfer from the Ag nanoparticles to the PS layer as the high lying free carrier levels of the Ag nanoparticles overlaps the absorption band of PS[3].

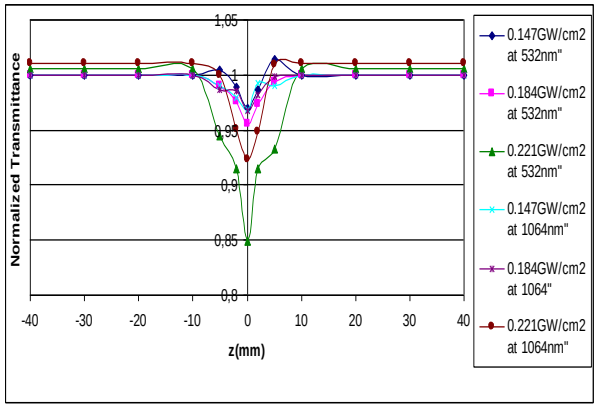

Fig. (10): Open-aperture Z-Scan for 0.058 weight ratio of composite

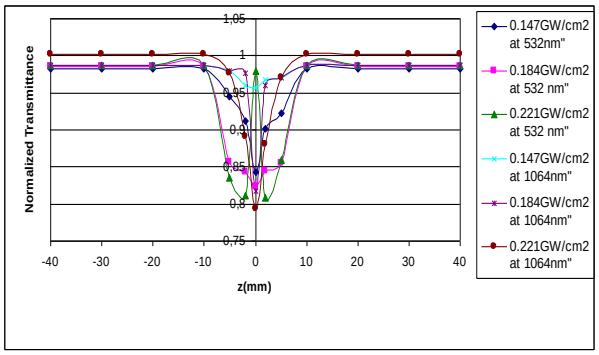

Fig. (11): Open-aperture Z-Scan for 0.038 weight ratio of composite

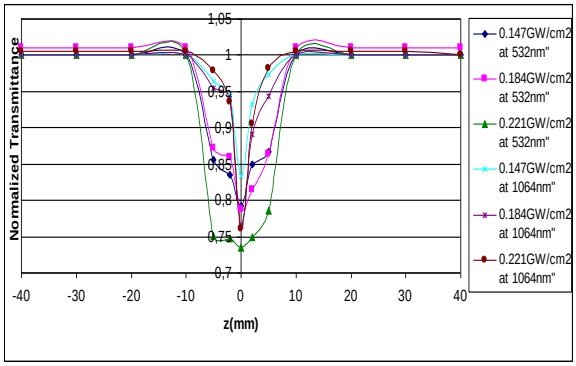

Fig. (12): Open-aperture Z-Scan for 0.078 weight ratio of composite

In the case of silver nanoparticles film 0.058 weight ratio of filler in Figure (11) absorption takes place from the SPR band into the higher lying free carrier bands of Ag nanoparticles as the intensity is increased. At large input intensities, silver nanocomposite films show saturation of absorption as the free carriers decay fast into the SPR bands thereby reducing the absorption cross-section at 532 nm. This result is match well with that reported by Porel[3]. Figuers (13,14) summarized the relation between β and intensities at (532,and 1064) nm.

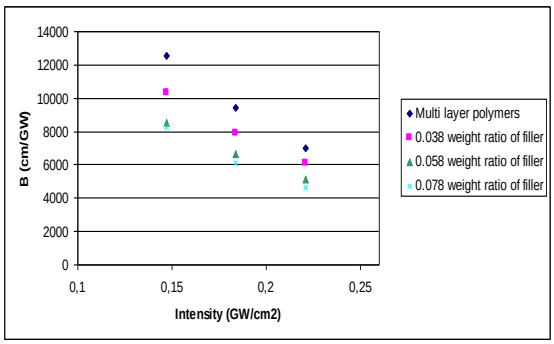

Fig. (13): The relation between the intensities and β at 532 nm

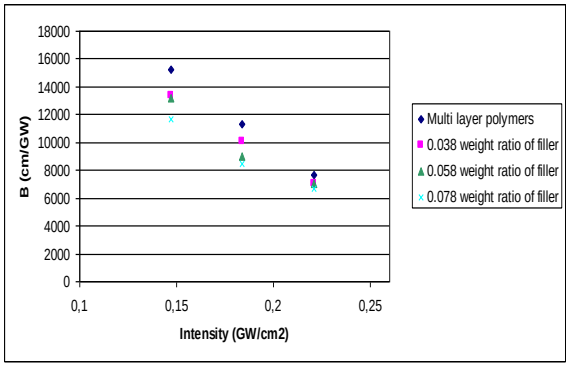

Fig. (14): The relation between the intensities and β at 1064 nm

The nonlinear absorption coefficient is inversely proportional to the weight ratio and the intensity. The relation between β and different weight ratio in multi layer polymers when added different weight ratio of filler at (532, 1064) nm can be shown in Figures (15, 16).

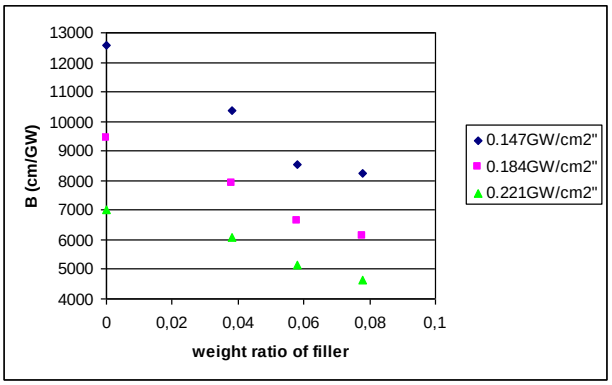

Fig. (15): The relation between the weight ratio of filler and β at 532 nm

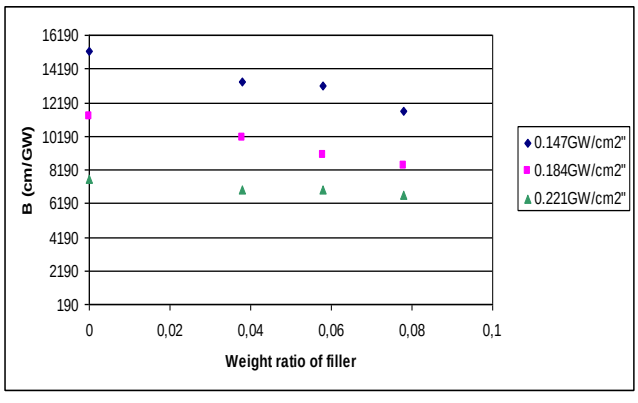

Fig. (16): The relation between the weight ratio of filler and β at 1064 nm

The limiting behavior of silver nanoparticels were performed. The output energy was plotted versus the input energy as measured for varoius

input energy. The limiting energy was measured at the focusing of a Gaussian beam and the beam waist. The limiting behavior was investigated by the closed-aperture Z-scan as shown in Figure 17.

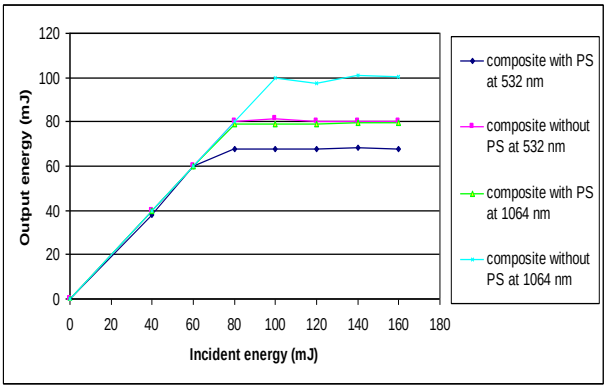

Fig. (17): Optical limiting behavior of silver nanoparticles

The output energies are increased as the incident energies increased until the limiting threshold energy where the output energy is constant inspit of the incident energies increasing. These energies are 80 mJ with a PS layer at 532 nm and 100 mJ without a PS layer at 1064nm and with a PS layer at 1064 nm also it is equal to 120mJ at 1064 nm without a PS layer. These energies values represent the optical limiting threshold energy for the samples as listed in the Table 1.

Table (1): The EL , Eclamping, and D.R values of the 0.058 silver nanocomposite with and without PS at 532 nm and 1064 nm.

Material	E_D (mJ)	E_L (mJ)	$E_{clamping}$ (mJ)	*D.R*
Composite with PS(poly styrene) At 532 nm	120	80	68	1.50
Composite without PS(poly styrene) At 532 nm	120	100	81.2	1.20
Composite with PS(poly styrene) At 1064 nm	160	100	79.77	1.60
Composite without PS(poly styrene) At 1064 nm	60	120	97.77	1.33

The damage threshold of the sample was tested to invistigate the bearing resistivity of the sample against high laser intensities. Figure (18) shows the laser induced damage at 120 mJ for 532 nm for 30 shots in sites by optical microscope pictures with 1000x magnification. The damage region shows a circular geometry in accordance to the spatial gaussian intensity distribution. Images represent several circular geometry. The first one a white circle, followed by a black one finally a brown.

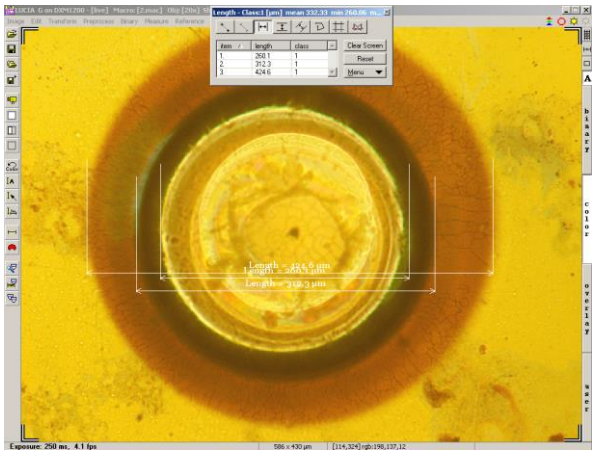

Fig. (18): Represents the hole diameter of 0.058 weight ratio of filler at 532 nm for 30 shots

The white circle represent that the bond of Ag-polymer is broken. Where the black color represents the carbonization effect. The brown represent the tail of laser pulse. For a high number of pulses the central irradiated region are more color as a result of the located movement of polymeric chains may be changed and the intermolecular forces like VanderWaals forces are weakened and may be broken then the conjugated bonds formed. For all these high intensity shots,the sample didn,t affect.This result is match well with the result reported by AL.Yasry [15].

Conclusions

Some conclusions can be extracted from the experimental results are summarized as follow:- The particle size of the silver inside the polymer is affected by the weight ratio of the filler. The nonlinear refractive index is directly proportional to the incident intensities ,and weight ratio of the filler. The nonlinear absorption coefficient is inversely proportional to the incident intensities, and weight ratio of the filler. The silver nanocomposite can be used as an excellent optical limiter. The presence of a

PS (poly styrene) layer will enhance the optical limiting behavior of the silver nanocomposite.

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سلوك المحدد البصري لنماذج من جزيئات الفضة ذات الدقائق النانومترية المشوبة لرقائق بوليمرية

رواء أحمد فارس زينب فاضل مهدي حسين علي جواد داود عبيد الطيفي

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الخلاصة في الدراسة الحالية تمت دراسة الخواص البصرية اللاخطية وخواص المحددات البصرية لمتراكبات الفضة النانوية المحضرة . تم تحضير العينات بأستخدام الطريقة الكيمياوية القياسية بنسب وزنية مختلفة (٠,٠٣٨، ٠,٠٥٨، ٠,٠٧٨). للتعرف على خصائص العينة تم اجراء عدة فحوصات مختبرية تتضمن :- فحوصات تركيبية وفحوصات بصرية ولغرض التعرف على الخصائص اللاخطية للعينات أستخدمت تقنية المسح على المحور الثالث بأستخدام ليزر النديميوم- ياك النبضي بأمد نبضة مقدرة ب٣٠ نانوثانية. أجريت التجارب بأستخدام ثلاث قيم للطاقة الداخلة للطوليين الموجيين (٥٣٢) نانومتر و(١٠٦٤) نانومتر ،وعلى جزئيين: الجزء الاول بأستخدام ثقب ضيق أمام الكاشف لغرض قياس معامل الانكسار اللاخطي والجزء الثاني بتكبير فتحة الثقب لغرض دراسة معامل الامتصاص اللاخطي. حيث بينت التجارب بأن معامل الانكسار يتناسب طرديا مع زيادة النسبة الوزنية للمالئات بينما معامل الأمتصاص اللاخطي يتناسب عكسيا مع زيادة النسبة الوزنية للمالئات وهذا السلوك اللاخطي يكون اكثر تأثيرا عند الطول الموجي (٥٣٢) نانومتر من (١٠٦٤) نانومتر وأن شدة امتصاص الالكترون الثنائي والتبعثر اللاخطي هما المسؤولان عن خواص المحددات البصرية الجيدة في متراكبات الفضة ذات الجزيئات النانومترية بدون حدوث تلف في العينة . كما اثبتت التجارب قوة عمل العينة لنبضات ليزرية عالية الشدة وعدم تاثرها. واوضحت التجارب أمكانية عمل عينات الفضةالنانوية كمحددات بصرية فعالة.