Jurnal
Teknologi

Full Paper

USING Z-SCAN TECHNIQUE TO MEASURE THE NONLINEAR OPTICAL PROPERTIES OF PMMA/ZnO NANOCOMPOSITES

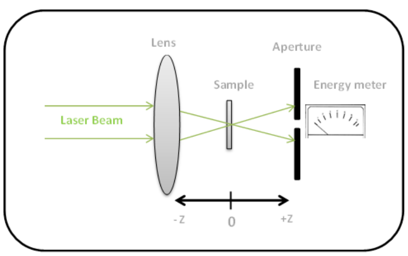
Haider Mohammed Shanshool[a,c*], Muhammad Yahaya[a], Wan Mahmood Mat Yunus[b], Ibtisam Yahya Abdullah[a,d]

[a]School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[b]Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM, Serdang, Malaysia
[c]Laser and Optoelectronics Research Center, Ministry of Science and Technology, Baghdad, Iraq
[d]Department of Physics, College of Science, University of Mosul, Iraq

Article history
Received
15 August 2015
Received in revised form
15 November 2015
Accepted
30 December 2015

*Corresponding author
haidshan62@gmail.com

Graphical abstract



Abstract

The study of nonlinear optical properties of polymer nanocomposites has been given increasing attention due its application in laser, communication and data storage technology. There is a need to enhance the understanding of all photonics technologies. In the current work, PMMA-ZnO nanocomposites as foils and as thin films have been successfully prepared. Casting method and spin coating were used to prepare them respectively. Nanocomposites were prepared by mixing ZnO nanoparticles with polymethyl methacrylate (PMMA) as the polymer matrix. Different contents of ZnO nanoparticles were used as the filler in the nanocomposites. The absorbance spectra of the samples were obtained. The linear absorption coefficient was calculated. The nonlinear refractive index and nonlinear absorption coefficient were investigated using a single beam Z-scan technique. A Q-switched Nd-YAG pulsed laser (532 nm, 7 ns, 5 Hz) was used as a light source. Both thin film's and foil's samples showed peak absorption at 375 nm and increasing absorption with ZnO nanoparticles concentration. The nonlinear refractive index was in the order of 10^{-11} cm^2/W for thin film samples and 10^{-12} cm^2 /W for foil's samples with a negative sign. In contrast, the nonlinear absorption coefficient is in the order of 10^{-6} cm/W and 10^{-7} cm /W for thin film and foil respectively. The figures of merit W and T were calculated in order to evaluate the suitability of the samples as optical switching device .However; they unsatisfied the requirements of optical switching devices but they can be considered as an excellent candidate for optical limiting.

Keywords: PMMA/ ZnO, Nanocomposite, Nonlinear refractive index, Nonlinear absorption coefficient

Abstrak

Kajian sifat optik taklinear bagi polimer nanokomposit telah semakin meningkat tumpuan kerana pengunaannya dalam laser, komunikasi dan teknologi simpanan data. Oleh itu telah menjadi keperluan untuk mempermudahkan kefahaman bagi semua Teknologi fotonik. Dalam kerja ini. Nanokomposit PMMA/ZnO sebagai foils dan filem tipis telah berjaya disediakan. Kaedah casting dan salutan putaran masing-masing telah digunakan dalam persediaan itu. Nanokomposit telah disediakan melalui percampuran zarahnano ZnO dengan polimetilmetailkrailat (PMMA) sebagai matriks polimer. Kandungan berbeza nanozarah ZnO telah digunakan sebagai filler dalam nanokomposit. Spektra penyerapan sampel–sampel telah diperolehi. Pekali penyerapan linear telah dikirakan, Indek pembiasn taklinear dan pekali penyerapan taklinear telah dikaji menggunakan teknik z-imbasan alur tunggal. Laser denyut Nd:YAG Q-suis (532 nm, 7 ns, 5 Hz) telah digunakan sebagai sumber cahaya. Kedua-dua filem tipis dan sampel foil telah menunjukan puncak penyerapan pada 375 nm dan bertambah penyerapan dengan kepekatan zarahnano ZnO. Index pembiasan taklinear dalam anggaran 10^{-11} cm^2/W untuk sampel filem tipis dan 10^{-12} cm^2 /W untuk sampel foil dengan tanda negatif. Sebaliknya pekali penyerapan taklinear dalam anggaran 10^{-6} cm/W dan 10^{-7} cm /W masing-masing untuk filem tipis dan foil. Parameter W dan T dikira untuk menilai kesesuaian sampel sebagai alat suiz optik. Walaubagaimanapun, sampel tidak dapat memenuhi keperluan sebagai alat suiz optk. Tetapi dapat dipertimbangkan sebagai calon cermerlang bagi pembatasan optik.

Kata kunci: PMMA/ZnO, indeks pembiasan tak linear, pekali penyerapan tak linear

1.0 INTRODUCTION

Currently, nanosize materials have been getting research interest due to the difference in their properties from those of bulk form. Many scientists' have been focused on the polymer inorganic nanocomposites. Those nanocomposites are the type of composite materials that combine the inorganic nanoparticles and polymer. Attention to study the linear and nonlinear optical properties of polymer-ZnO nanocomposites depend on their applications in optical devices.

Zinc oxide is one of the most attractive oxide semiconductors due to its uniqueness in electrical and optical properties. Beside its other important features like biocompatibility, long-term environmental stability, non-toxicity and low cost [1]. ZnO has a wide band gap (3.37 eV) which makes it an efficient UV absorber. Due to its large exciton binding energy (60 meV) which is much larger than the room temperature thermal energy (26 meV), ZnO becomes a promising material for optoelectronic devices of short wavelength, especially for UV laser diode and light-emitting diodes.

PMMA earned unlimited care and significant attributes because of its unique properties such as rigid, hard, high transparency in the visible region, low optical absorption, thermal capability, electrical performance, excellent mechanical properties, low cost, simple synthesis and low refractive index. PMMA is a favourite as a matrix to contain the components due to its good outdoor weather resistance and resistance to hydrolysis. It is a thermoplastic, so it can be designed as anything we want [2, 3]. Besides, it can be probably used in nonlinear optics as a nanocomposite. PMMA has a low nonlinear refractive index, n_2; so it cannot be used alone as an NLO medium [4].

In spite of many studies, there is a need to enhance the understanding of all photonics technologies, and contribute to have the knowledge about the suitability to use nonlinear optical materials as optical switching and optical limiting, especially the common usage of optical detectors, and sensors for different scientific purposes [1]. There is a need for optical limiting devices to protect the photosensitive components from high intensity of laser radiation. Optical limiting is defined as a nonlinear optical process in which the transmittance of the material decreases with the increase of incident light intensity.

In the present work, nanocomposites of PMMA/ZnO, both as foils and thin films, have been successfully prepared by spin coating and casting method respectively. The linear absorption spectra and linear absorption coefficient are evaluated. Using a single beam Z-scan technique, the nonlinear optical properties of the samples are investigated and compared. To the best of our knowledge, there is no report published describing the preparation of PMMA/ZnO nanocomposites as foils for that purpose.

2.0 EXPREMENTAL

PMMA/ZnO nanocomposites with different concentrations of ZnO were prepared in two steps. Firstly, the PMMA solution was prepared by adding the chloroform ($CHCl_3$) to the poly (methyl methacrylate) (PMMA) which was supplied by Sigma-Aldrich. 80 mg of PMMA was dissolved in 1.024 mL of chloroform using a sonicator for 15 minutes, then the magnetic stirrer (angular velocity of 400 rpm and timed for one hour at room temperature) was used to help in dissolving and prevent agglomerates. Secondly, zinc oxide (ZnO) was purchased from Sigma-Aldrich. Nanoparticles (50 < size < 100 nm), with various concentrations (0, 1, 3, 5, 10 and 15 wt %) were added to the mixture of PMMA/chloroform. Then, the sample was sonicated for 15 min to disperse the nanoparticles in the solution. After that, the solution was stirred at room temperature for one hour by a magnetic stirrer (angular velocity 400 rpm) to get a homogeneous solution. To prepare the nanocomposites as foil by using the casting method, the solution was cast uniformly on a glass petri dish at room temperature. After 30 min, the film was removed as a foil easily. After that, the foil was kept at room temperature for one day for solidification. Later, the foils of pure PMMA and nanocomposites (PMMA/ZnO) of different concentrations were collected.

By using spin coating method (0.2 mL of mixture, angular velocity of 800 rpm, and timed 30 sec), thin film was prepared on quartz substrate (2 cm x 2 cm) which was washed with detergent, and cleaned with methanol. After that, it was washed in acetone by sonicating each for 10 minutes. Afterwards, substrates were rinsed with distilled water, and then dried in hot air. The solvent was then allowed to evaporate inside the lab at room temperature, until a dried thin film of pure PMMA and PMMA/ZnO nanocomposites of different concentrations were obtained.

The linear transmittance spectra values of the samples were measured using UV-vis spectrophotometer (PerkinElmer instruments-Lambda 900 UV/VIS Spectrometer). The setup of Z-scan technique used in the present measurement is shown in Figure 1. A Q-switched Nd:YAG pulse laser (from Beijing Mini laser Technology Co., Ltd.), giving the second harmonic at 532 nm (7 ns, 5 Hz) was used as the light source. A 10 cm lens was used to focus the laser beam. The energy of transmitting light in the far field, which passed through the aperture, was recorded by energy meter.

In the single beam z-scan technique, the sample moved [5] along the Z-axis, which represents the focus of a Gaussian laser beam, while the transmittance, as a function of the sample position relative to the beam focus, was recorded by a detector through the aperture in the far field. The sample, which acted as a thin lens due to the nonlinear refraction, changed the beam dimensions. These changes were translated into variations of transmittance energy by the aperture. Then, the information provided was used to determine the nonlinear refractive index of the sample. Moreover, when the aperture was removed, the differences of the transmittance energy as a result of the nonlinear absorption would provide sufficient information to determine the nonlinear absorption coefficient of the samples.

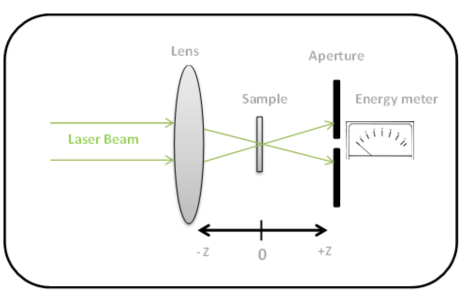


Figure 1 Z-scan experiment setup

3.0 RESULTS AND DISCUSSION

3.1 Absorption Spectra

Figure 2 (a) and (b) show the UV-visible absorption spectra of PMMA and PMMA/ZnO nanocomposites as thin films and foils. The PMMA (pure) has low absorbance in both UV as well as in the visible region, but the PMMA/ZnO nanocomposites have high absorbance in the UV region, indicating the absorption peak at 375 nm belonged to the behaviour [6] of Zno nanoparticles. This means it is able to absorb in the UVA range (320-400 nm). This has been demonstrated in details in our other text [7]. The peak of absorbance increased when the content of ZnO nanoparticles increased due to the nano –size of ZnO that increases the surface area, so strong absorption occurred [8]. Besides that, the peak in the foil samples was higher than thin film samples for the same content of ZnO.

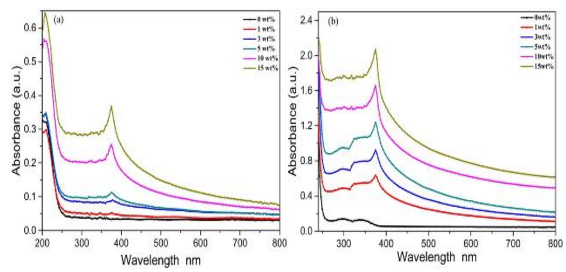


Figure 2 Absorption spectra of PMMA/ZnO nanocomposites, (a) as thin film and (b) as foil

3.2 Linear Absorption Coefficient

The linear absorption coefficient (a) for thin film samples was calculated using the equation [8, 9]:

$$\alpha = \frac{1}{d}\, ln\frac{1}{T} \qquad (1)$$

While the linear absorption coefficient (a) for foil samples was calculated using the equation [10]:

$$\alpha = \frac{1}{d}\ ln\ \frac{(1-R)}{T} \qquad (2)$$

Where d is the thickness of the sample, T is the transmittance, and R is the reflectance that was obtained from the data of UV-visible spectroscopy.

The thickness of the thin film samples was determined by the FESEM image cross section; it was around 800 nm, while the thickness of the foil determined using a digital micrometer at different places in each film and an average was taken, it was around 70 µm.

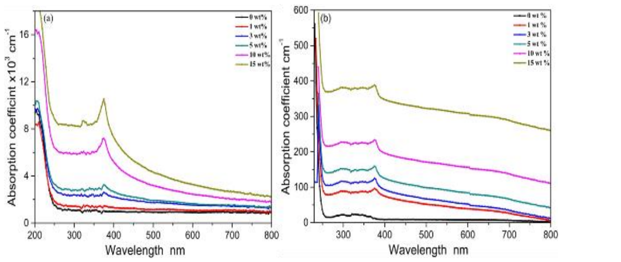


Figure 3 Linear absorption coefficient of PMMA/ZnO nanocomposites as (a) Thin film (b) Foil

Figure 3 (a) and (b) show the linear absorption coefficient (α) spectra of PMMA (pure) and PMMA/ZnO nanocomposites as thin films and foils. α depends on the wavelength of light that is actually absorbed. The values of absorption coefficient α for thin film samples were much more than the values of foil samples. It was around 1000 times greater, that is because α is inversely proportional to the thickness of the sample. The thickness of the foil was around 100 times the thickness of the thin film. The highest value of α was showed in the thin film samples in the UV region but less than it was observed at the visible region. Meanwhile the foil samples indicated low deference to the value of a between two regions. All samples showed decrement in the value of α with increasing of wavelengths; however, it seemed gradually in foils but faster in thin films. The results showed that α increased as the content of ZnO nanoparticles increased in the nanocomposites, especially at short wavelengths.

3.3 Nonlinear Optical Properties

3.3.1 Z-Scan Technique (Opened & Closed Apertures)

The radius of the beam at the focus was calculated to be 26.6 µm. The Rayleigh length Z_o was estimated by [5, 11]:

$$Z_\circ = \frac{\pi w_o^2}{\lambda} \tag{3}$$

Z_o is 4.17 mm. It was greater than the thickness of the samples, which is an important requirement for Z-scan technique. The procedures described by Sheik-Bahae *et al*., [12-14] were used to analyse the obtained data.

The high nonlinear effect in the present work belonged to the ZnO nanoparticles. The PMMA pure had a negligible nonlinear optical response at 532 nm when it was measured using the same technique. Those results are corresponded to the previous literatures [15, 16].

3.3.1.1 Closed Aperture, Nonlinear Refraction

The total refractive index, n can be calculated by [17]:

$$n = n_\circ + n_2 I \tag{4}$$

where n_o is the linear refractive index, and n_2 is the nonlinear refractive index related to the intensity, I. The units of intensity is taken as m^2 /w or cm^2 /w.

In order to determine the nonlinear refractive index, n_2 of the PMMA/ZnO nanocomposites as foil and thin film, Figure 4 is referred. The figure shows the measurements of both foil and thin film of the normalized transmittance versus the sample position in the closed-aperture z-scan for low (1wt %) and high (15wt %) concentration of ZnO nanoparticles in the polymer matrix. The other concentration (3 wt %, 5 wt % and 10 wt %) showed the same traces. A peak followed by a valley were the hallmark of the negative nonlinear refractive index in PMMA/ZnO nanocomposites .This is due to the self-defocusing [5]. Thus, the figures demonstrated that the samples exhibited self-defocusing effect, i.e., they have a negative nonlinearity.

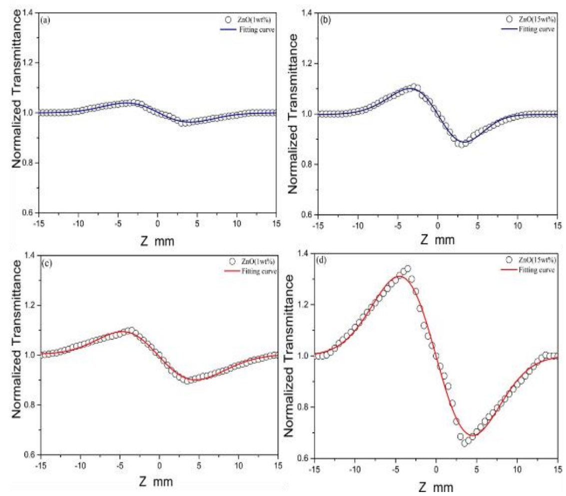


Figure 4 The normalized transmittance as a function of sample position in the closed aperture Z-scan for PMMA/ZnO nanocomposites; (a) as Thin film with ZnO(1wt%), (b)as thin film with ZnO(15wt%), (c) as Foil with ZnO(1wt%), (d) as Foil with ZnO(15wt%)

From Figure 4, the distance between the peak and valley (ΔZ_{P-V}) was found to be 7 mm compared to (ΔZ_{P-V} = 1.7 Zo). This indicates a satisfy [13, 18-21] condition of third-order nonlinearity. Therefore, this confirms the presence of pure electronic third-order nonlinearity. Besides that, it is clear that the z-scan trace changed as the concentration of ZnO nanoparticles was changed. This caused a difference in the nonlinear phase shift which in turn changed the value of the nonlinear refractive index, n_2. Hence, the magnitude of n_2 depends on the concentration of ZnO nanoparticles in the nanocomposites. It is clearly shown in Figure 5.

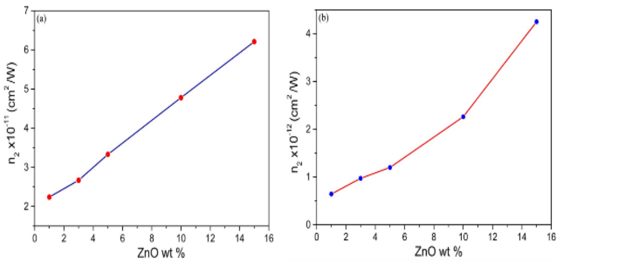


Figure 5 Nonlinear refractive index n_2 as a function of ZnO wt% ; (a)as a thin film and (b)as foil

By using the variable transmittance values of the closed-aperture z-scan, the nonlinear phase shift $\Delta\Phi_\circ$ and the nonlinear refractive index n_2 were determined.

$\Delta\Phi_\circ$ can be calculated by [4,13]:

$$\Delta\Phi_\circ = \frac{\Delta T_{P-V}}{0.466(1-S)^{0.25}} \quad (5)$$

ΔT_{p-v} is the change in transmittance between the peak and the valley in a closed aperture Z-scan, and is defined as:

$$\Delta T_{P-V} = T_{P-} T_V \quad (6)$$

where T_p and T_v are the normalized transmittance of the peak and valley as seen in Figure 4 .

The ratio of the light passing through the aperture to the light in front of the aperture is defined as S linear transmittance of aperture. The details of equations and calculations were mentioned in other text [22]. Selecting the size of aperture can help to produce better results. S is 0.2, which followed the most reported experiments [14] that used 0.1< S< 0.5. Thus the values of $\Delta\Phi_\circ$ can be calculated and were used to calculate the nonlinear refractive index, n_2 by using [4, 5]:

$$n_2 = \frac{\lambda\,\Delta\Phi_\circ}{2\,\pi I_\circ\, L_{eff}} \quad (7)$$

Where λ is wavelength of the laser source; I_o Irradiance of the laser beam at the focus which was calculated before, and L_{eff} the effective length of the sample.

3.3.1.2 Open Aperture, Nonlinear Absorption

The absorption of the material *A* is intensity dependent and is given by [17]:

$$A = \alpha + \beta I \quad (8)$$

where β is the nonlinear absorption coefficient related to the intensity I and α is linear absorption coefficient. By removing the aperture, open aperture z-scan is used to study the nonlinear absorption coefficient. During this process, the transmitted beam was collected by the detector without any limitation.

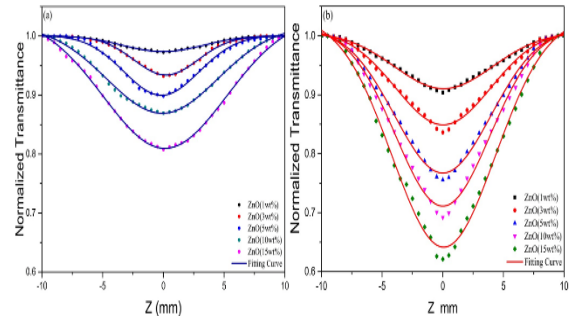


Figure 6 The normalized transmittance as a function of the sample positioned in the open aperture Z-scan for PMMA/ZnO (a) as a thin film (b) as a foil

Figure 6 shows an open-aperture z-scan for both thin film and foil. It used to explore the nonlinear absorption coefficient. Transmittance is sensitive to the nonlinear absorption. The transmittance has a minimum value at the focus, and then increases steadily on both sides of the focus. That represents a valley. This valley with high concentration of ZnO nanoparticles was deeper than the low concentrationof both, thin film and foil samples. This indicates that the high concentration exhibits stronger nonlinear absorption than low concentration. By the same way, the valley in foil samples was deeper than in thin film for the same concentration of ZnO nanoparticles. A symmetric valley refers to the positive nonlinear absorption coefficient β, which represents the two-photon absorption. The two-photon absorption causes the change in the transmittance of the samples [17]. From the data, for both samples thin film and foil, it is clear that the PMMA/ZnO nanocomposites is a two photon absorber. During the calculation of energy gap, it was shifted to the lower value as the ZnO concentration was increased. Here, the shifted [23] energy gap enhanced two photon absorptions. Thus, the results of the open aperture z-scan showed that the nonlinear absorption coefficient values were enhanced by increasing the concentration of ZnO nanoparticles, which is clearly shown in Figure 7, and it is in agreement with the results obtained by Haripadmam *et al*., [11] and Sreeja *et al*. [24].

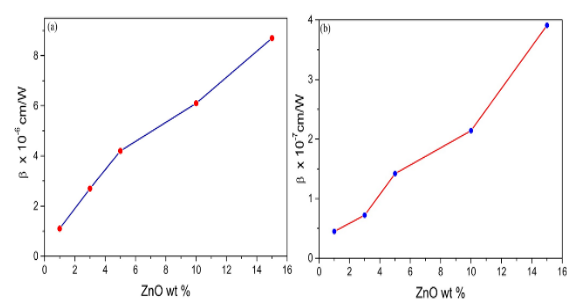


Figure 7 Nonlinear absorption coefficient β as a function of ZnO wt% (a) as thin film (b) as foil

The nonlinear absorption coefficient β, is determined by [17, 25]:

$$\beta = \frac{2\sqrt{2}\,\Delta t}{I_o L_{eff.}} \qquad (9)$$

where Δt is the one valley value that was obtained from the data of the open Z-scan curve. The values of $\Delta\Phi_{\circ}$, L_{eff}, β and n_2 of PMMA/ZnO nanocomposites as thin films and foils are listed in Table 1 and Table 2.

Table 1 Optical properties of PMMA/ZnO nanocomposites thin film

Nanocomposites as Thin Film	PMMA/ ZnO 1wt%	PMMA/ ZnO 3wt%	PMMA/ ZnO 5wt%	PMMA/ ZnO 10wt%	PMMA/ ZnO 15wt%
$L_{eff.}$ x 10^{-5} cm	7.5840	7.4798	7.4304	7.1365	6.8603
β X 10^{-6} cm/W	1.1188	2.7310	4.2295	6.1652	8.7039
Δ $\Phi_{\circ}$	0.1815	0.2178	0.2722	0.3630	0.4765
n_2 x 10^{-11} cm^2/W	-2.251	-2.739	-3.447	-4.786	-6.534

Table 2 Optical properties of PMMA/ZnO nanocomposites foil

Nanocomposites as Foil	PMMA/ ZnO 1wt%	PMMA/ ZnO 3wt%	PMMA/ ZnO 5wt%	PMMA/ ZnO 10wt%	PMMA/ ZnO 15wt%
$L_{eff.}$ x 10^{-3} cm	5.9454	5.6798	5.1139	4.1394	2.8052
β X 10^{-7} cm/W	0.4757	0.7747	1.4137	2.1258	4.2572
Δ $\Phi_{\circ}$	0.4084	0.6353	0.7261	1.1572	1.4522
n_2 x 10^{-12} cm^2/W	-0.646	-1.052	-1.336	-2.630	-4.870

Table 1 and 2 show the values of L_{eff}, $\beta, \Phi_{\circ}$ *and* n_2 of thin film and foil samples. The values of these parameters were different from the nanocomposites samples as thin film and foil due to the nonlinear refractive index and nonlinear absorption coefficient which depend on the linear absorption coefficient α, in addition to other parameters. The value α depends on the thickness of the sample which is different between the thin film and foil. For PMMA/nanocomposites as thin films, α is usually in the order of 10^3 or more, while in the case of samples as foils, it is in the order of 10^2.

3.3.2 The Suitability of Samples as Optical Switches and Optical Limiter

The suitability of the samples to be used as optical switches was evaluated through two figures of merit *W* and *T* [26, 27, 28]:

$$W = \frac{n_2 I}{\alpha_o \lambda} \qquad (10)$$

$$T = \frac{\beta\lambda}{n_2} \qquad (11)$$

where n_2 *is* nonlinear refractive index, β is nonlinear absorption coefficient, α_o is linear absorption coefficient; λ *is* wavelength of laser source; and I is the irradiance of the laser beam. The required conditions should be satisfied in terms of *W*>>1 and *T*<<1.

When the above equations were applied on the PMMA/ZnO nanocomposites as thin film and foil. The values of W and T are unsatisfied the required conditions. So, these samples are not suitable to be used as optical switching devices at a wavelength of 532 nm.

The suitability of the sample to be used as optical limiting depends on the sign and the value of nonlinear refractive index, n_2. Besides, the presence of strong nonlinear absorption produces good optical limiting [29]. The negative sign of n_2 indicates a satisfaction of the sample. Hence suitable to be used as an optical limiter for laser radiation due to the self – defocusing, which means it will diverge the radiation. According to the results obtained, the sign n_2 of PMMA/ZnO nanocomposites, for both thin film and foil, was negative. Hence, they are considered as a promising candidate to be used as optical limiter devices at wavelength of 532 nm [30].

4.0 CONCLUSION

Foils and thin films of pure PMMA and nanocomposites PMMA/ZnO with different concentrations of ZnO nanoparticles were prepared successfully. The foil thickness was 70 µm, while thin film thickness was 800 nm. UV-visible tests showed high absorbance of UV radiation by PMMA/ZnO depending on the content of ZnO. All nanocomposites have an absorption peak at a wavelength of 375 nm which belongs to ZnO nanoparticles, which increased with the concentration of ZnO. The nonlinear refractive index is a negative sign in PMMA/ZnO nanocomposites as the thin films and foils. This is due to self-defocusing. The presence of third-order nonlinearity was confirmed with the condition (ΔZ_{P-V} = 1.7 Zo) was satisfied. The magnitude of n_2 and β depend on the concentration of ZnO nanoparticles in the nanocomposites. Both thin film and foil are unsatisfied the suitability to be used as optical switching. However, they indicated the suitability to be used as optical limiting.

Acknowledgments

The authors would like to acknowledge the contribution and the financial support by the Malaysian Ministry of Higher Education and Universiti Kebangsaan Malaysia under research grant (FRGS/1/2013/SG02/UKM/01/1).

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