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luizno.bjp@gmail.com
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Mohammed Shanshool, Haider; Yahaya, Muhammad; Mat Yunus, Wan Mahmood; Yahya Abdullah, Ibtisam
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CONDENSED MATTER

Measurements of Nonlinear Optical Properties of PVDF/ZnO Using Z-Scan Technique

Haider Mohammed Shanshool[1,3] · **Muhammad Yahaya**[1] · **Wan Mahmood Mat Yunus**[2] · **Ibtisam Yahya Abdullah**[1,4]

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Abstract The nonlinear optical properties of ZnO nanoparticles dispersed in poly (vinylidene fluoride) (PVDF) polymer are investigated. PVDF/ZnO nanocomposites were prepared by mixing different concentrations of ZnO nanoparticles, as the filler, with PVDF, as the polymer matrix, using casting method. Acetone was used as a solvent for the polymer. FTIR spectra of the samples were analyzed thus confirming the formation of α and β phases. The absorbance spectra of the samples were obtained, thereby showing high absorption in the UV region. The linear absorption coefficient was calculated. The single-beam Z-scan technique was used to measure the nonlinear refractive index and the nonlinear absorption coefficient of the PVDF/ZnO nanocomposite samples. We observed that the nonlinear refractive index is in the order of 10^{-13} cm^2/W with the negative sign, whereas the nonlinear absorption coefficient is in the order of 10^{-8} cm/W.

Keywords Nonlinear optical properties · PVDF/ZnO nanocomposite · Z-scan technique

✉ Haider Mohammed Shanshool
haidshan62@gmail.com

1 School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

2 Department of Physics, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Malaysia

3 Ministry of Science and Technology, Baghdad, Iraq

4 Department of Physics, College of Science, University of Mosul, Mosul, Iraq

1 Introduction

Recently, a new research area using polymeric nanocomposites emerged and gained considerable attention. The syntheses of polymer nanocomposites, which include the nanometric inorganic materials, are considered an integral aspect of polymer nanotechnology. Depending on the presence of the inorganic materials, these nanocomposites have been improved and offered particular properties variety than pure polymer. In polymer science, polyvinylidene fluoride (PVDF) has been the center of scientific interest. It is a semicrystalline polymer which has a special feature that distinguishes it from other polymers, i.e., its uncommon polymorphism. It shows five crystalline phases, namely α, β, γ, δ, and ε [1]. The properties of PVDF offer a wide range of scientific and technological applications such as optical switches, optical waveguides, light-emitting diodes, lenses, and nonlinear optical devices [2]. Besides that, the nonlinear quality of PVDF can be significantly improved by hosting nanoparticles of high nonlinear optical susceptibility [3].

Zinc oxide is one of the most attractive semiconductors due to its unique combination of electrical and optical properties [4]. ZnO is considered a nonlinear optical nanomaterial [2]; therefore, using its nanoparticles as the filler in PVDF can enhance the nonlinear optical properties of the polymer. Our previous report [5] revealed that adding inorganic nanoparticles such as ZnO into organic polymer such as PVDF can enhance the optical properties of the polymer due to interfacial interactions between them.

A single-beam Z-scan technique is one of the different measurement techniques [6] used for the determination of nonlinear optical properties of materials. In the single-beam Z-scan technique, the sample is moved [6] 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, is recorded by a detector—through the aperture in the far field. The sample, which acts as a thin lens due to the nonlinear refraction, changes the beam dimensions. These changes were translated into variations of the transmitted energy by the aperture. Then, the provided information 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 nonlinear absorption would provide sufficient information to determine the nonlinear absorption coefficient of the sample. One of the important features of this technique is that the separation between nonlinear refraction and nonlinear absorption is easily distinguished.

In the present work, pure PVDF and PVDF/ZnO nanocomposites as films were prepared via casting. Acetone was used as the solvent for the polymer. The linear and nonlinear optical properties of nanocomposites were investigated. To the best of our knowledge, there was no report published on the nonlinear optical properties of pure PVDF and PVDF/ZnO nanocomposites using a single-beam Z-scan technique.

2 Method

Preparation of PVDF/ZnO nanocomposites was done as follows: Firstly, the PVDF solution was prepared by adding a suitable solvent, i.e., acetone. To prepare 2 wt% of PVDF/acetone, 8 mg of polyvinylidene fluoride (PVDF), purchased from Sigma-Aldrich, was dissolved in 0.492 ml of acetone. The PVDF/acetone solution was kept on a magnetic stirrer at an angular velocity of 400 rpm, temperature 60 °C, and time 30 min to help dissolve. Secondly, to prepare the nanocomposite PVDF/ZnO with different concentrations of ZnO (1, 3, 5, 8, and 10 %), ZnO (50<size<100 nm), purchased from Sigma-Aldrich, were added to a mixture of PVDF/acetone. Then, a sonicator was used for 15 min to disperse the nanoparticles in the solution. After that, the solution was stirred at room temperature for 1 h with an angular velocity of 400 rpm by a magnetic stirrer to get a homogeneous solution. The deposition of the solution had been done by casting method which was used to prepare pure PVDF and PVDF/ZnO films by pouring the prepared solution onto a quartz substrate as shown in Fig. 1. The solvent was then allowed to evaporate inside the lab at room temperature, until the dried samples of pure PVDF and nanocomposites (PVDF/ZnO) of different concentrations were obtained.

The linear absorption spectra values of the present samples were measured using a UV-Vis spectrophotometer (PerkinElmer Instruments-Lambda 900UV/VIS Spectrometer).

The setup of the Z-scan technique used in the present measurement is shown in Fig. 2. A Q-switched Nd:YAG pulse laser, from (Beijing Mini Laser Technology Co., Ltd.), giving 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 an energy meter.

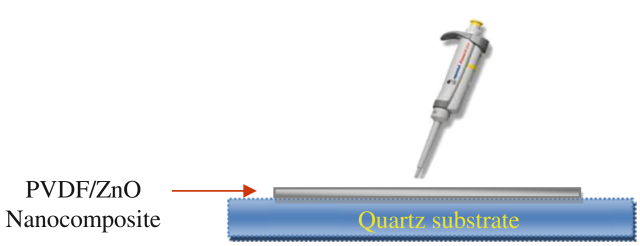

Fig. 1 PVDF/ZnO nanocomposite prepared by casting method

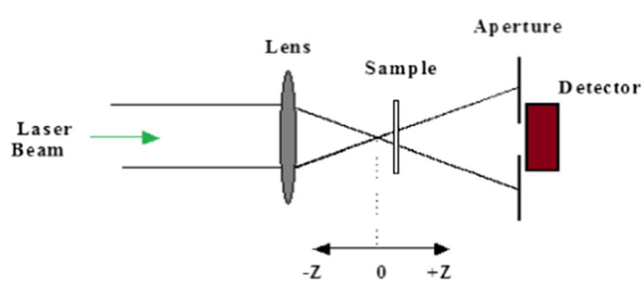

Fig. 2 Setup for Z-scan measurements

3 Results and Discussion

3.1 UV-Visible Spectra; Absorption Spectra

Figure 3 demonstrates the UV-visible absorption spectra of pure PVDF (0 wt%) and PVDF/ZnO nanocomposites of different concentrations of ZnO nanoparticles (wt%). The absorption spectrum of pure PVDF is limited in the UV region, but it enhances when adding the ZnO nanoparticles that have high energy gap [7]. The curves of the nanocomposites of high ZnO concentration show a clear peak in the UV region and less absorption in the visible region. The peak of the high absorption at approximately 375 nm was observed. The peak absorption of ZnO nanoparticles corresponded to the result obtained by Indolia and Gaur [2]. In addition, the lower absorption in the UV and visible regions were due to the roughness of the surfaces that increased with increasing ZnO concentrations, which caused scattering and then loss of incident intensity [8].

3.2 FTIR Analysis

The samples of pure PVDF and PVDF/ZnO nanocomposites were checked by FTIR spectroscopy,(brand, Perkin Elmer; range, 4000–650 cm^{-1}; resolution, 4 cm^{-1}). The FTIR spectra, whereby the transmittance mode, of PVDF films in the range 650–4000 cm^{-1} are shown in Fig. 4. According to previous works, the peaks at 766, 795, 974, and 1402 cm^{-1} were

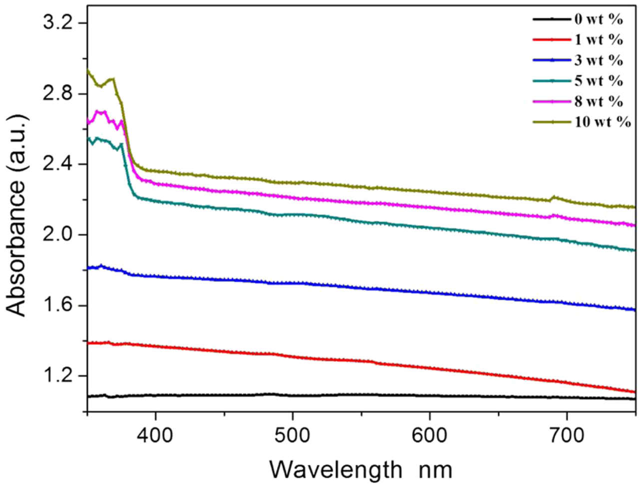

Fig. 3 Absorption of pure PVDF and PVDF/ZnO nanocomposites

identified as the α phase, while the ones at 840 cm^{-1} and 1275–1279 cm^{-1} were identifications of the β phase [9, 10]. Also, the one at 3021 cm^{-1} corresponds to the β phase [9]. The IR vibration modes due to the γ-phase are at 833, 1171, and 1233 cm^{-1}. Vibrational bands at 766 c m^{-1} are the CF_2 bending and skeletal bending mode while at 795 cm^{-1} is the CH_2 rocking mode; the peaks at 840 cm^{-1} are the CH_2 rocking mode [11, 12]. The 840-cm^{-1} band is common to the β and γ phases; a sharp and well-resolved band indicates the β phase, whereas a broadband indicates the γ phase. The broadband is due to imbrication, in which the 833-cm^{-1} band often appears as a shoulder [10, 13]. The peak at 1404 cm^{-1} represents a typical vibrational band which corresponds to the deformed vibration of the CH_2 group [8]. Besides that, the literatures indicated that ZnO nanoparticles have stretching and bending bands but they appear to be suppressed. The literature revealed that the bands are between 360 and 420 cm^{-1} [14] or near 420 cm^{-1} [15], or at 468 and 480 cm^{-1} [16] or near 438 cm^{-1} [17].

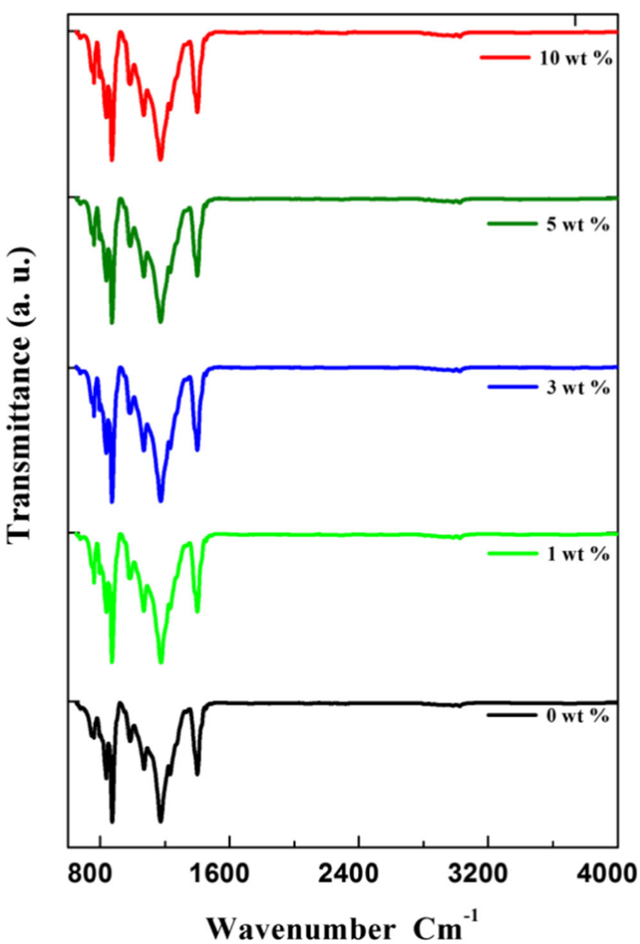

Fig. 4 FTIR spectra of pure PVDF and PVDF/ZnO nanocomposites

3.3 Calculation of Linear Absorption Coefficient (α)

The linear absorption coefficient (α) of the samples was calculated by [18]:

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

where d is the thickness of the film, T is the transmittance, and R is the reflectance. The thickness of the film was measured by FESEM cross section; it was 9.5–9.9 μm. The values of reflectance and transmittance were obtained from the data of UV-Vis.

Figure 5 demonstrates that α depends on the wavelength of light that was absorbed. The pure PVDF sample has a lower value of α than the nanocomposites samples due to the effect of ZnO nanoparticles. The absorption coefficient increased with the increase of ZnO nanoparticles concentration. Since the ZnO nanoparticles have low transmittance and high absorbance in the UV region, the nanocomposites samples showed higher value of α in the UV region as compared with that in the visible region.

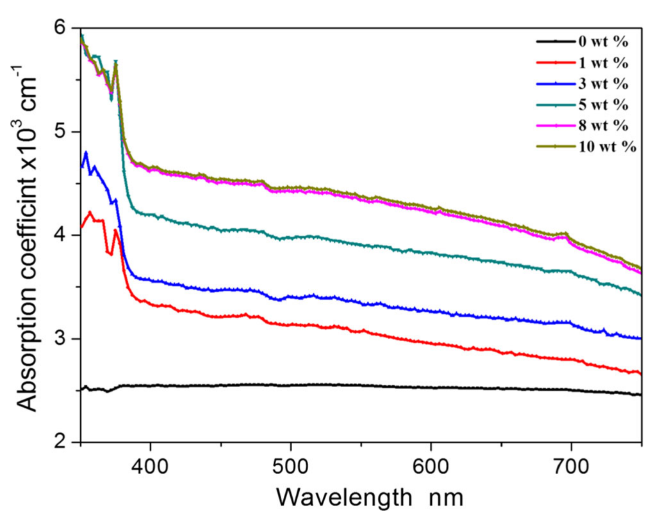

Fig. 5 Absorption coefficient α for pure PVDF and PVDF/ZnO nanocomposites

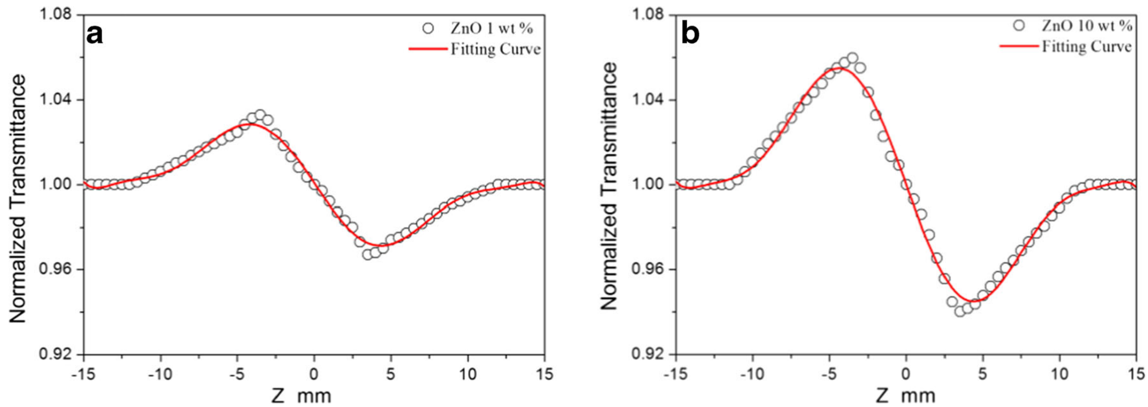

Fig. 6 **a**, **b** The normalized transmittance as a function of sample position in closed-aperture Z-scan for PVDF/ZnO

3.4 Nonlinear Optical Properties

3.4.1 Z-Scan Technique (Opened and Closed Apertures)

The radius of the beam at the focus was calculated to be 26.6 μm. The irradiance of the laser beam at the focus, I_o=12.78 GW/cm^2. The Rayleigh length is Z_o= 4.17 mm. It is greater than the thickness of the samples, which is an important requirement for the Z-scan technique [6, 19].

The procedures had been described by Sheik-Bahae et al [20–22] and were used to analyze the obtained data.

The high nonlinear effect observed in the present work belonged to the ZnO nanoparticles, whereas the pure PVDF and quartz substrate had negligible nonlinear optical response at 532 nm when measured by the same technique. This work, to our best knowledge, is considered as the first work to study the nonlinear optical properties of PVDFs as pure and nanocomposite polymer; therefore, the results could not be compared with previous literatures.

3.4.2 Closed Aperture; Nonlinear Refraction

In order to explore the nonlinear refractive index n_2, Fig. 6 shows the measurements of the normalized transmittance versus sample position in the closed-aperture Z-scan for low (1 wt%) and high (10 wt%) concentration of ZnO nanoparticles in the polymer matrix. The other concentrations (3, 5, and 8 wt%) all showed the same traces. A peak followed by a valley is the hallmark of a negative nonlinear refractive index in PVDF/ZnO nanocomposites, which was due to self-defocusing [23]. So, the figures demonstrate the samples exhibiting a self-defocusing effect, i.e., they have negative nonlinearity.

There are electronic and thermal effects on the nonlinear refractive index. However, the separation between them is not easy [24, 25].

In our experiments, the laser radiation with low repetition rate (5 Hz) has been used, thus a cumulative thermal effect was prevented [26].

From Fig. 6, the distance between peak and valley ($\Delta Z_{\text{P–V}}$) was found approximately 7 mm, when compared to ($\Delta Z_{\text{P–V}}$=

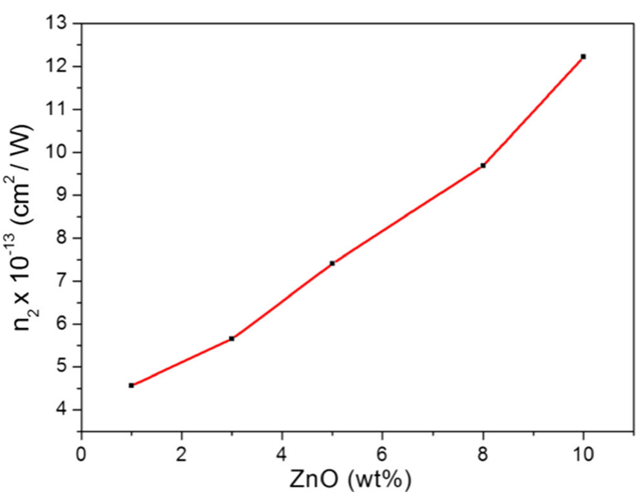

Fig. 7 Nonlinear refractive index n_2 as a function of ZnO wt%

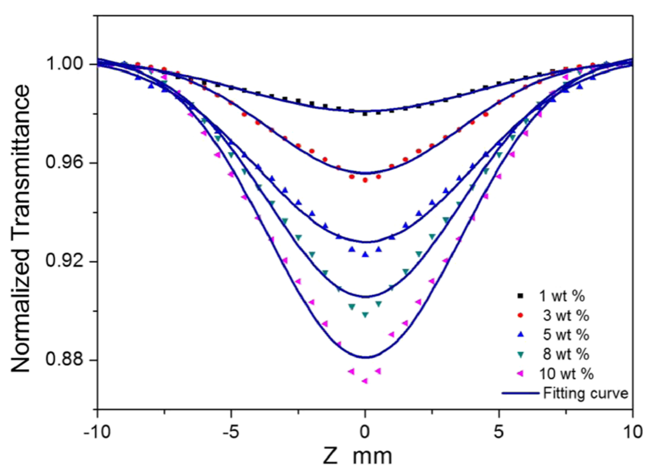

Fig. 8 The normalized transmittance as a function of sample position in open-aperture Z-scan for PVDF/ZnO nanocomposites

Table 1 Values of L_{eff}, β,$\Phi_\circ$, and n_2 for PVDF/ZnO nanocomposites

Nanocomposites	PVDF/ZnO 1 wt%	PVDF/ZnO 3 wt%	PVDF/ZnO 5 wt%	PVDF/ZnO 8 wt%	PVDF/ZnO 10 wt%
$L_{eff.}\times 10^{-4}$ cm	3.0405	2.8294	2.4778	2.2489	2.2339
β cm/W$\times 10^{-8}$	2.064	5.21	9.636	14.24	17.58
$\Delta\Phi_\circ$	0.147	0.17	0.192	0.231	0.29
n_2 cm^2/W$\times 10^{-13}$	−4.562	−5.652	−7.408	−9.684	−12.22

1.7 Z_o), which satisfied [21, 27–30] the condition of third-order nonlinearity, thus confirming the presence of pure electronic third-order nonlinearity. Besides that, it was clear that the Z-scan trace differed as the ZnO nanoparticles concentration was changed, which caused a difference in the nonlinear phase shift which, in turn, changed the value of the nonlinear refractive index n_2. Therefore, the magnitude of n_2 depended on the concentrations of ZnO nanoparticles in the nanocomposites and is clearly shown in Fig. 7.

By using variable transmittance values of 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 [21, 31]:

$$\Delta\Phi_\circ = \frac{\Delta T_{P-V}}{0.466(1-S)^{0.25}} \tag{2}$$

$\Delta T_{p\ v}$ is the change in transmittance between the peak and valley in a closed-aperture Z-scan, which can be defined as:

$$\Delta T_{p\ v} = T_p - T_V \tag{3}$$

where T_p and T_v are the normalized peak and valley transmittances as seen in Fig. 5.

The ratio of the light passing through the aperture to the light in front of the aperture [32] is defined as S. In other words, S is linear transmittance of aperture, which can be calculated as [31]:

$$S = 1 - \exp\left(-2r_a^2/w_a^2\right) \tag{4}$$

r_a is the radius of the aperture; w_a is the beam waist on the aperture.

To obtain better results, the aperture size was chosen using S=0.2, which is followed by the most viable value as reported from previous experiments [22], i.e., 0.1<S<0.5.

Hence, the values of $\Delta\Phi_\circ$ can be calculated and was then used to calculate the nonlinear refractive index n_2 by the equation [31, 33]:

$$n_2 = \frac{\lambda\Delta\Phi_\circ}{2\pi I_\circ L_{eff}} \tag{5}$$

λ is the wavelength of the laser source. $I_\circ$ is the irradiance of the laser beam at the focus as calculated before. L_{eff} is the effective length of the sample and calculated as [19, 21]:

$$L_{eff} = \frac{1-e^{-ad}}{a} \tag{6}$$

α is the linear absorption coefficient; d is the thickness of the sample.

The values of $\Delta\Phi_\circ$,$L_{eff,}$ and n_2 of PMMA/ZnO nanocomposites are listed in Table 1.

3.4.3 Open Aperture; Nonlinear Absorption

Removing the aperture resulted in an open-aperture Z-scan which was then used to investigate the nonlinear absorption coefficient, during which the transmitted beam was collected by the detector without any limitation.

In order to explore the nonlinear absorption coefficient, Fig. 8 shows the open-aperture Z-scan. The transmittance is sensitive to nonlinear absorption. The transmittance has a minimum value at the focus, and then increased steadily on both sides of the focus. That represents a valley. That valley for high ZnO nanoparticles concentration is deeper than that of low concentration. This indicates that high concentration exhibits stronger nonlinear absorption performance than low concentration. A symmetric valley indicates positive nonlinear absorption coefficient β, which represents the two-photon

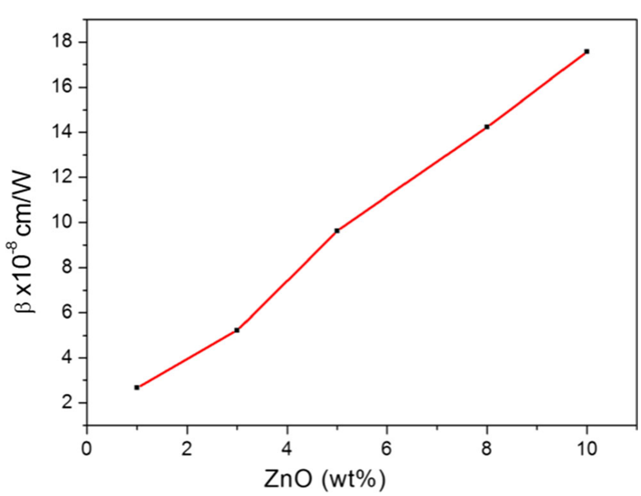

Fig. 9 β as a function of ZnO wt% for PVDF/ZnO nanocomposites

absorption. The two-photon absorption caused the change in the transmittance of the samples [34].

From the data, it was clear that the PVDF/ZnO nanocomposite is a two-photon absorber. In addition, the results of the open-aperture Z-scan showed that the nonlinear absorption coefficient values were enhanced with the increase in the ZnO nanoparticles concentration, which is clearly shown in Fig. 9.

To determine the value of nonlinear absorption coefficient β, the following equation [34, 35] was used:

$$\beta = \frac{2\sqrt{2}\Delta t}{I_o L_{\mathrm{eff}}} \tag{7}$$

where Δt is the one valley value that was obtained from the data of the open Z-scan curve.

The values of β that were calculated from Eq. (7) for different concentrations of ZnO nanoparticles in nanocomposites are listed in Table 1.

4 Conclusion

Films of pure PVDF and nanocomposite PVDF/ZnO with different concentrations of ZnO nanoparticles have been prepared successfully via casting. UV-visible spectroscopy had showed high absorbance for UV radiation by PVDF/ZnO depending on the content of ZnO nanoparticles. From the analysis of the FTIR spectra, the presence of α and β phase of the polymer was confirmed. The value of the absorption coefficient of pure polymer was lower than that of nanocomposites. It had also been found to increase with the increase of the weight percentage of ZnO nanoparticles.

The nonlinear refractive index had a negative sign, which was due to self-defocusing. The presence of the third-order nonlinearity had been confirmed as the condition ($\Delta Z_{\mathrm{P-V}}$= 1.7 Zo) was satisfied. The magnitude of n_2 with the negative sign and β were in the order of 10^{-13} and 10^{-8} cm/W, respectively. They were dependent on the concentrations of ZnO nanoparticles in the nanocomposites.

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