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# The effect of doping acid on the third-order nonlinearity of carboxymethyl cellulose by the Z-scan technique

A. Jafari*, R. Naderali, H. Motiei

*Atomic and Molecular Group, Department of Physics, Faculty of Science, Urmia University, Iran*

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The studies on the third-order nonlinear optical properties of carboxymethyl cellulose nanocomposite in the absence and presence of inorganic acid as a dopant was reported. The Z-scan technique was used to measure the nonlinear refraction $n_2$, and absorption $\beta$, indexes and the third-order nonlinear susceptibility $\chi^3$. Characterization of this nanocomposite was performed by using scanning electron microscopy and Ultraviolet–Visible absorption spectroscopy in two different solvents; Dimethylformamide and N-Methylpyrrolidone. Additionally X-ray diffraction was used to study their crystal structure. The measured values of the nonlinear refraction of each sample in both of the solutions were in the order of $10^{-9} m^2/w$ and the corresponding third-order nonlinear susceptibilities were in the order $10^{-4}$ esu.


## 1. Introduction

Conductive polymers are a new chapter in chemistry, and have attracted much attention in recent years. They have the ability to react through highly reversible oxidation and reduction reactions [1]. Polyaniline (PANI) is one of the most important conductive polymers due to its optical, electrical and molecular properties [2,3] and its application in solar cells, electronic covers, electrochemical screens [4] and rechargeable batteries [5]. Polyaniline is based on conductive polymers have low physical and mechanical strength, low solubility and unabsorbability, which have led to problems in commercial applications [6]. Polyaniline has applications in composite polymers such as its utilization as a conductive polymer in rechargeable batteries, removing chrome from wastewater at plating industries and so on. The composite of polyaniline with biopolymers such as chitosan, carboxymethyl cellulose (CMC) etc. is a new class of natural materials that have physicochemical properties [7,8]. Cellulose is important in constructing deflectable polymers. By using CMC in composites and increasing their polar properties and also increasing these natural polymers in the polyaniline matrix, certain results were observed without changing the properties of the polymer such as modification of thermal properties, increasing solubility and conduction. In comparison to micro particles, nano particles have a higher surface area to volume ratio and high surface reaction activity. Therefore, interaction with other particles within the mixture will be enhanced while strength, heat resistance and etc. will increase. Therefore, we have decided to consider a nanoscale form of CMC in the presence of polyaniline. These nano materials are widely employed in optoelectronics, electronics, medicine and photonics [9–11]. We can also find various potential technological applications such as serving as an active material in electro-optical devices, modulators and optical switches [12]. Various physical properties of composite polymers are important including multi photon absorption, free carrier absorption, nonlinear scattering and refraction [13,14] and their third order nonlinearity. Nonlinear properties of graphen oxide-carboxymethyl cellulose composite films [15] and carboxymethyl starch [16] have been considered, recently. We want to investigate the nonlinear optical parameters of the samples in steady-state conditions. Considering that high power pulse lasers create temporary states. Therefore, the experimental conditions are satisfied by low-power lasers and hence the continous wave laser was

* Corresponding author.
*E-mail address:* a.jafari@urmia.ac.ir (A. Jafari).

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preferred over the high power pulsed laser. In this experimental work, the nonlinear optical properties of a new nanocomposite by using the Z-scan technique were investigated. Recently, lasers in the continuous wave (CW) regime and low powers have been extensively used to identify the threshold nonlinearity of materials [17–20]. The nonlinear refraction and absorption coefficients were extracted. Then, the results were carefully discussed in terms of the effect of solvent and existing inorganic acid. This paper includes the following sections: The theory of the Z-scan technique and the principles of experimental measurements including X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Ultraviolet–Visible absorption (UV–Vis) are presented in Section 2. The results and discussion about the nonlinear optical absorption and refraction of the nanocomposite in the absence and presence of an inorganic acid and the comparison of them in two different solvents are presented in Section 3. A conclusion is presented in Section 4.

## 2. Experiment

### 2.1. NLO measurements

The Z-scan technique has been used in order to investigate the third order nonlinear optical properties of the nanocomposite CMC on PANI,. This technique [21] exhibits simplicity, high sensitivity and an ability to determine the sign and magnitude of nonlinear coefficients [22]. The light source used in the experiment was a Nd-YAG laser beam with a wavelength of 532 nm in a continous wave (CW) regime. The experimental setup of the Z-scan is depicted in Fig. 1, where BS is a beam splitter. The laser beam has a Gaussian spatial distribution that is tightly focused by using a 10 cm focal length lens. The beam waist at the focused spot is about 327 μm. The corresponding Rayleigh length $Z_0$, is about 63.08 mm. Thus the thickness of the sample cuvette, 6.89 mm, is less than the Rayleigh length (i. e. $L < Z_0$). Therefore the thin-sample approximation is valid. By moving the sample through the focus, the change in the far field intensity with and without an aperture is recorded as a function of the sample's position. In the closed aperture technique, the transmittance change and any nonlinear phase shift due to the Kerr lens generated in the material through an aperture was accurately monitored by photodiode 1. The system was calibrated using $CS_2$ as the reference. Also, the nonlinear coefficients of pure solvents were measured. Although NMP has a higher nonlinearity than DMF, it was found to be several orders of magnitude smaller than the nonlinear coefficients of our sample. So permissible we ignored them.

### 2.2. X-ray diffraction

The XRD spectra of pure polyaniline and composite (polyaniline/carboxymethyl cellulose) in the absence and presence of excess

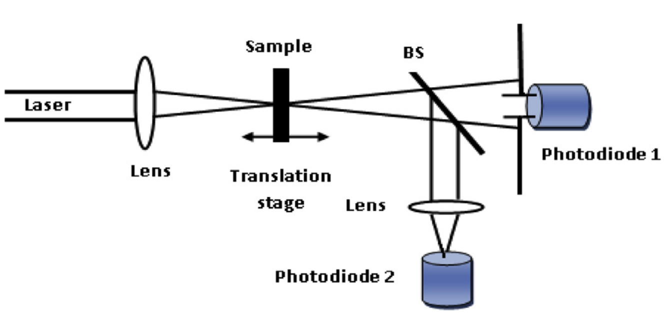


**Fig. 1.** Scheme of the experimental setup of the Z-scan technique.

inorganic acid as a dopant are shown in Figs. 2–4. These X-ray patterns were recorded using an Xpert Philips diffractometer. According to the figures, The semi-crystalline structure of PANI was shown. Comparing between spectra, it can be observed that the crystallite of the composite increased. So it can be concluded that the presence of cellulose in solutions and templates had a significant effect on increasing the crystallite of the composite. The broad diffraction peaks confirm the nano crystalline nature of the sample. Particle size of these nanoparticles are calculated by the Debye-Scherrer formula $d = k\lambda/\beta\cos\theta$, where $k$ is a constant ($k = 0.93$) and $\beta$ is the width of the diffraction peak at half maxima. The average particle size of the nanocomposite in the absence and presence of acid is found to be 19.20 nm and 95.73 nm, respectively, which indicates the formation of well-defined semi crystalline nanostructures.

### 2.3. Scanning electron microscopy

The results of the SEM for the composite (PANI/CMC) in the absence and presence of excess acid as a dopant are shown in Fig. 5a and b, respectively. According to Fig. 5a, approximately surface homogeneity of composite are appeared and particles formed in bar and spherical shape that their diameter are in nanometric scale of polyaniline. The nanocomposite in the presence of acid are particularly spherical in shape.

### 2.4. UV–Vis absorption spectra

Fig. 6 a and b exhibit the linear absorption for the analyzed nanocomposite. Data was recorded using control solutions (DMF and NMP) and CMC in a quartz cell and then was depicted in related software by using a UV–Vis spectrometer (PG instruments Ltd-T80). According to the absorption spectrum, absorbance of CMC in the absence of acid in DMF and NMP at $\lambda = 532$ nm are 0.37 and 0.22, respectively. The absorption of CMC in the presence of acid in DMF and NMP are 0.61 and 0.21, respectively. The values of linear absorption can be determined by $\alpha = -1/d\ln T$ where $T$ is the transmittance of the sample at a given wavelength. The linear absorption coefficients of the composite (PANI/CMC) in the absence and presence of acid at $\lambda = 532$ nm in DMF and NMP are listed in Table 1. For the CMC samples with and without inorganic acid, the change of the solvent from DMF to NMP will affect the absorption of the nanocomposite. Since linear absorption of a nanocomposite with NMP is higher than the samples with DMF, it is expected that the observed nonlinear properties in the samples have a thermal origin. So it is anticipated that nonlinearity in solutions including NMP to be higher than solutions including DMF. Since absorption is reduced in focus, therefore, the two-photon absorption phenomenon occurs.

## 3. Results and discussion

Two kinds of experiments were performed. In the first experiment (A), CMC with and without acid was solved in a NMP solvent and in the second experiment (B), CMC was solved in a DMF solvent. Solutions were exposed to laser light. The amount of transmittance from the sample on the detector will vary due to the Kerr lens generated in the CMC by the intense beam. Since the laser has Gaussian distribution and the CW regime of the laser is used, nonlinearity during the Z-scan measurements may have a thermal origin in addition to the intensity dependent refractive coefficient and two photon absorption process. Experiments for nanocomposite with and without acid in both of the solvents have been repeated for three powers of laser. It was observed that by increasing intensity of laser beam, the peak-valley separation

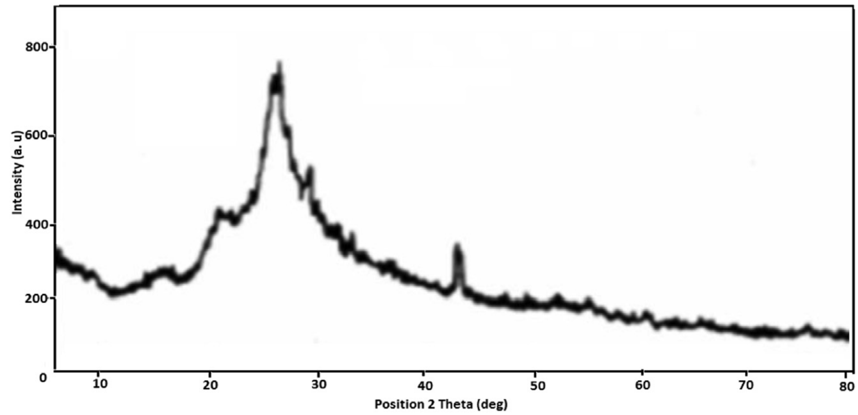


**Fig. 2.** The X-ray diffraction pattern of pure polyaniline.

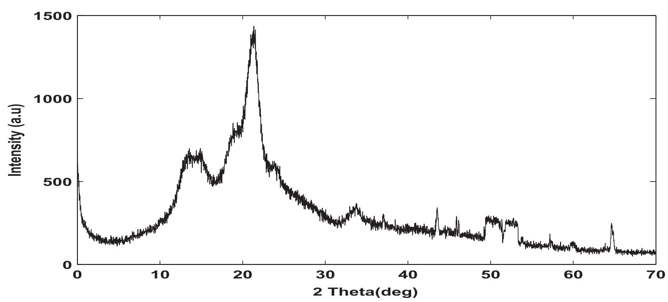


**Fig. 3.** The X-ray diffraction pattern of the composite (PANI/CMC) in the absence of an inorganic acid as a dopant.

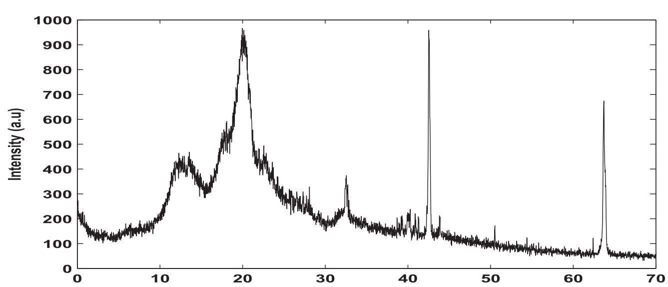


**Fig. 4.** The X-ray diffraction pattern of composite (PANI/CMC) in the presence of inorganic acid as a dopant.

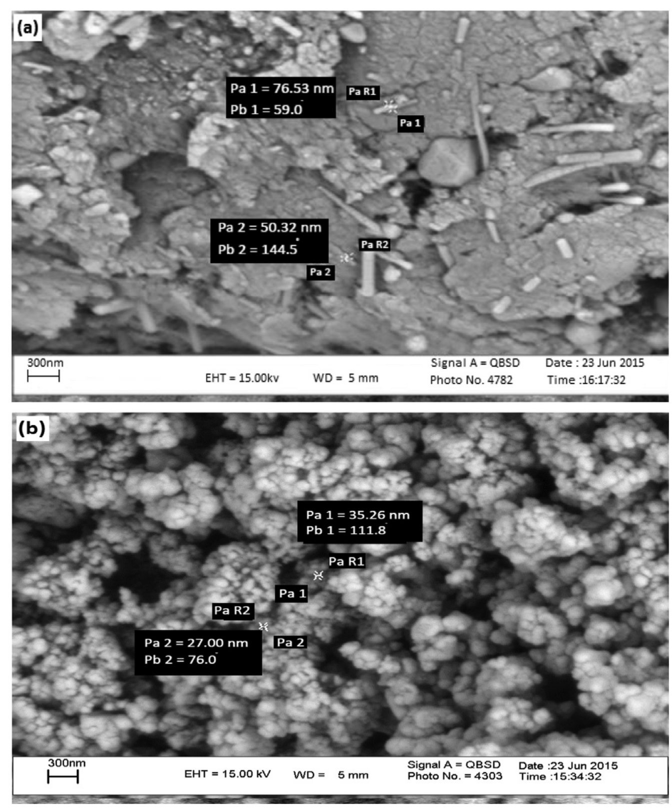


**Fig. 5.** The SEM image of composite (PANI/CMC) (a) in the absence of excess inorganic acid and (b) in the presence of excess inorganic acid.

increases that indicates the thermal effect in nonlinear behavior of CMC nanocomposite. Closed aperture curves display the composite (PANI/CMC) in the absence and presence of excess inorganic acid, that solved in two different solvents. The curves was shown just in one intensity to compare efficiently the effect of solvent and acid. Fig. 7a and b display closed aperture Z-scan curves of the composite (PANI/CMC) in the absence and presence of excess inorganic acid, that solved in two different solvents. According to these figures that the peak-valley patterns indicate negative nonlinearity with a self-defocusing behavior. Magnitude and the sign of the nonlinear phase shift can be determined from changes in normalized transmittance and the position of the peak and valley, [23,24].

$$n_2 = \frac{\Delta T_{P-V}}{0.406(1-S)^{0.25} k I_0 L_{eff}} \tag{1}$$

where, $\Delta T_{(P-V)}$ is the difference between peak and valley transmission, S corresponds to aperture in linear transmittance, $k = 2\pi/\lambda$ ($\lambda$ is the laser wave length) is the wave vector, $I_0$ is the intensity of the laser beam at the focus ($z = 0$), $L_{eff} = 1 - e^{-\alpha L}/\alpha$ is the sample's effective length and $\alpha$ is the linear absorption coefficient. $S$ can be determined using:

$$S = 1 - \exp\left(\frac{-2r_a^2}{\omega_a^2}\right) \tag{2}$$

Here, $\omega_a$ is the beam radius on the aperture and $r_a$ is the aperture radius. The XRD and SEM spectra were used to measure the size of particles. Also, the influence of inorganic acid on the nanocomposite, as seen in Figs. 4 and 5b, show that by adding acid the nonlinearity of nanocomposites (according to calculated values of

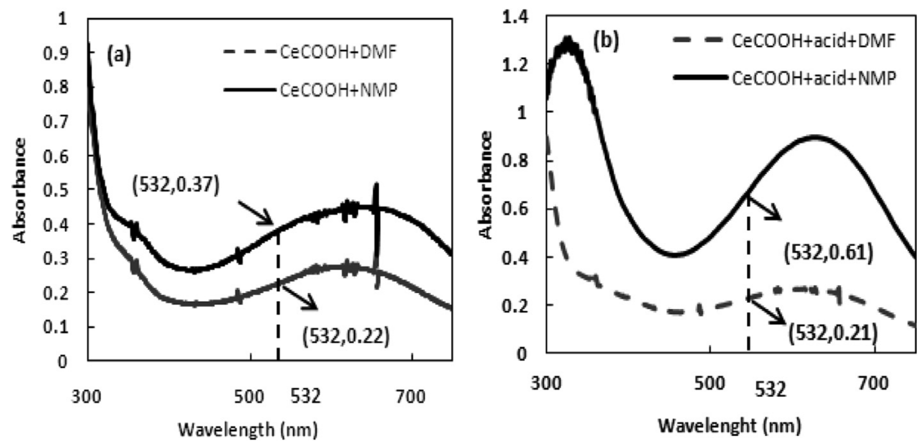


**Fig. 6.** The absorption spectra of the CeCOOH nanocomposite (a) in the absence of excess inorganic acid and (b) in the presence of excess inorganic acid, solved in DMF and NMP, respectively.

**Table 1**
The linear absorption coefficients and third-order nonlinear optical coefficients of CMC in the absence and presence of inorganic acid in two different solvent (DMF and NMP) in the intensity $I_0 = 56.22$ kw/m$^2$ for$\beta$ and $I_0 = 48.91$ kw/m$^2$ for $n_2$.

| Sample | Linear absorption coefficient, $\alpha$(cm$^{-1}$) | Nonlinear absorption coefficient, $\beta_{eff}$($\times 10^{-3}$ m/w) | Nonlinear refraction coefficient, $n_2$($\times 10^{-9}$ m$^2$/w) |
|---|---|---|---|
| CMC without acid + DMF | 0.507 | 2.45 | −0.787 |
| CMC without acid + NMP | 0.853 | 3.52 | −1.153 |
| CMC by acid + DMF | 0.484 | 1.62 | −0.606 |
| CMC by acid + NMP | 1.406 | 1.67 | −1.318 |

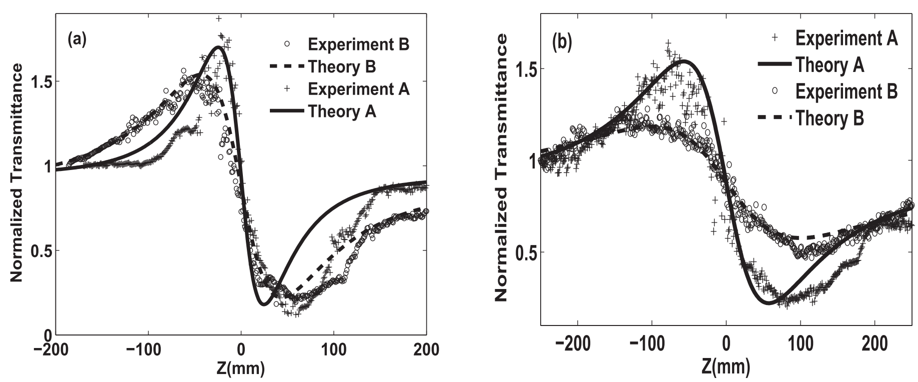


**Fig. 7.** The closed aperture Z-scan curves of the composite (PANI/CMC) (a) in the absence of excess inorganic acid and (b) in the presence of excess inorganic acid, solved in DMF and NMP, respectively. The solid and dashed lines depict a theoretical fit for the intensity 48.91 kw/m$^2$.

Table 1) decreases as the size of them increases. The reduced nonlinearity in the CMC with acid can be attributed to the appeared peaks in Fig. 4.

By analyzing the closed aperture Z-scan curves as we had predicted before, these figures illustrate that the solutions including NMP as a solvent have higher peak-valley transmittance difference $\Delta T_{(P-V)}$ and a higher nonlinear refraction coefficient value than the solutions including DMF as a solvent that were calculated and listed in Table 1. The theoretical fits of these curves is plotted using equation (3):

$$T(z) = 1 - \frac{4\Delta\varphi X}{\left(1+(X)^2\right)\left(9+(X)^2\right)} \quad (3)$$

Fig. 8a and b show the comparison between the absence and presence of excess inorganic acid in the composite. It is determined that in Fig. 8a, the CMC solution without acid have higher nonlinearity than the CMC solution with acid. While in Fig. 8b, the CMC solution without acid have lower nonlinearity than the CMC solution with acid. So, it can be concluded that NMP solvent change the effect of existing acid.

There are various reported mechanism that cause nonlinear absorption of nanoparticles, for example two-photon absorption (TPA), reverse saturable absorption (RSA), free carrier absorption (FCA) and nonlinear scattering [25,26]. Fig. 9a and b shows the effective nonlinear absorption coefficient of the nanocomposite in two different solvents. The linear and nonlinear absorption coefficients ($\alpha$,$\beta_{eff}$) of composite (polyaniline/carboxymethyl cellulose), soluble in DMF and NMP, are calculated. The effective nonlinear absorption coefficient $\beta_{eff}$(m/w) is obtained from a best fitting performed on the experimental and theoretical data of the open aperture measurement. The normalized change in transmitted intensity can be calculated using the following equation:

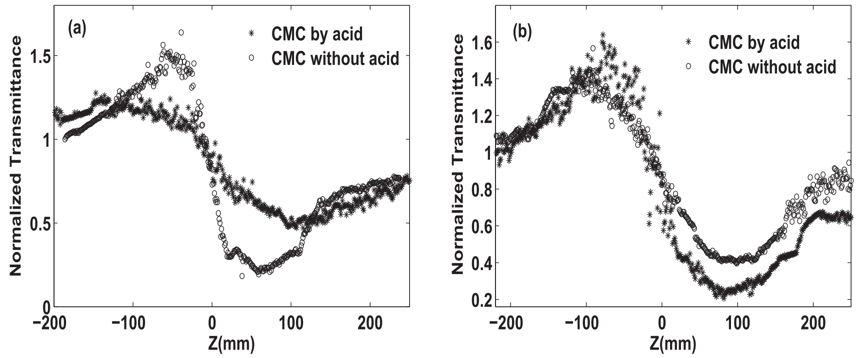


**Fig. 8.** The comparison of composite (PANI/CMC) in the absence and presence of excess inorganic acid solved in (a) DMF and (b) NMP, respectively.

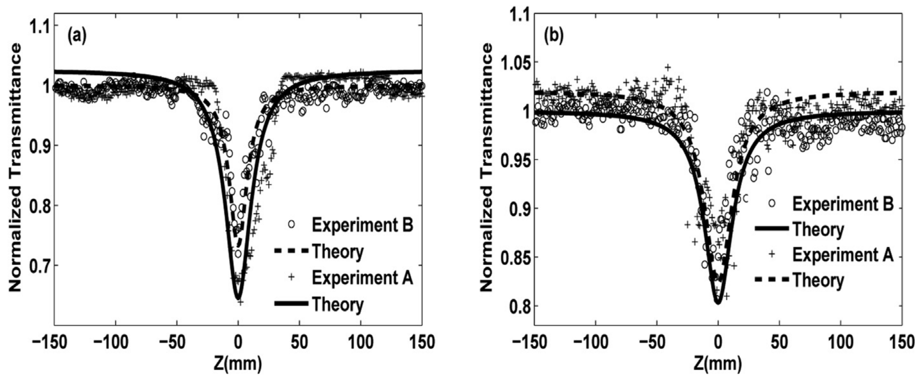


**Fig. 9.** The open aperture Z-scan curves of CeCOOH nanocomposite (a) in the absence of excess inorganic acid and (b) in the presence of excess inorganic acid, solved in DMF and NMP, respectively. The solid and dashed lines depict the theoretical fit for the intensity 56.22 kw/m$^2$.

$$T(z) \approx 1 - \frac{\beta_{eff} I_0 L_{eff}}{2\sqrt{2}} \frac{1}{\left(1 + (X)^2\right)} \tag{4}$$

where $T(Z)$ is the normalized transmittance of the sample at $Z$ and $X = Z/Z_0$ where $Z_0 = k\omega_0^2/2$ is the Rayleigh diffraction length and $\omega_0$ is the beam waist at the focal point $Z = 0$ and $Z$ is the sample's position [21,22]. Then the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^3$ and the magnitude of third-order nonlinear susceptibility are shown in Table 2 can be calculated using the following relations.

$$Re\chi^3(\text{esu}) = \frac{cn_0^2}{120\pi^2} n_2 \left(\text{m}^2/\text{W}\right) \tag{5}$$

$$Im\chi^3(\text{esu}) = \frac{c^2 n_0^2}{240\pi^2\omega} \beta_{eff}(\text{m/W}) \tag{6}$$

$$\left|\chi^3\right| = \left[\left(Re\left[\chi^3\right]\right)^2 + \left(Im\left[\chi^3\right]\right)^2\right]^{1/2}(\text{esu}) \tag{7}$$

where $n_0$ is the linear refractive index of each sample, c is the velocity of light and $\omega$ is the angular frequency of the light field. The figure of merit (FOM) of nanocomposites is given by $\chi^3/\alpha$, which is of the order of $(7.11–15.57)10^{-4}$ (esu cm), in this relation $\alpha$ is the linear absorption coefficient. These samples are good candidate for optical devices and optical limiters, medicine devices and etc.

## 4. Conclusion

In summary, two new composites (polyaniline/carboxymethyl cellulose) were prepared. The effects of the solvents and the presence of inorganic acid on the nonlinear properties of the nanocomposite were investigated by the Z-scan technique using a Nd:YAG laser. All the samples have a negative nonlinear refraction with self-defocusing behavior. The comparison between closed aperture curves showed that the samples solved in NMP have better nonlinearity than DMF solutions. Moreover in the comparison between the absence and presence of acid, the nonlinear

**Table 2**
The third-order nonlinear optical susceptibilities of CMC in the absence and presence of inorganic acid in two different solvent (DMF and NMP).

| Sample | Re$\chi^3$($\times 10^{-4}$ esu) | Im$\chi^3$($\times 10^{-4}$ esu) | $\|\chi^3\|$($\times 10^{-4}$ esu) |
|---|---|---|---|
| CMC without acid + DMF | −4.79 | 0.63 | 4.83 |
| CMC without acid + NMP | −7.48 | 0.97 | 7.54 |
| CMC by acid + DMF | −4.28 | 0.49 | 4.30 |
| CMC by acid + NMP | −9.99 | 0.54 | 10.01 |

refraction index of CMC solution without acid and DMF is more than that of the CMC solution with acid and DMF, on the contrary $n_2$ for the CMC solution without acid and NMP is less than that of the CMC solution with acid and NMP. The open aperture Z-scan curves reveal the effective nonlinear absorption caused by two-photon and excited state absorption. The values of $\beta$ can be extracted with corresponding experimental data and theory. The third-order susceptibility for all of the samples were also calculated. The composite materials because of short response time, high Kerr nonlinear susceptibility can be used as an optical switches, super-fast optical limiters, medicine devices and etc.

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