Nonlinear Optical Properties of Rigid Polyurethane Foam/SiO₂ Nanocomposite

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ABSTRACT—Polyurethane closed cell (PUCC)/SiO₂ nanocomposites have been prepared by using in situ polymerization approach. The third-order optical nonlinearities of PUCC/SiO₂ nanocomposites, dissolved in DMF are characterized by Z-scan technique at the measurement wavelength of 532 nm. The nonlinear refractive (NLR) indices and nonlinear absorption (NLA) coefficients of samples were calculated from closed and open aperture Z-scan in the order of 10⁻⁸ (cm²/W) with negative sign and 10⁻⁵ (cm/W), respectively. The origin of optical nonlinearity in this case may be attributed due to the presence of two photon absorption (TPA) effect. The synthesized samples were examined by optical microscopy, SEM imaging and Raman spectroscopy. All the results related to NLO properties, suggest that PUCC/SiO₂ may be a promising candidate for the nonlinear optical application in the visible region.

KEYWORDS: Nanoparticles, Nonlinearity, Polyurethane, Silica, Z-scan.

I. INTRODUCTION

Since nonlinear optics (NLO) cover a vast field of research with wide range of potential applications, such as optical limiting, all optical photonics and photoelectronics devices [1]–[3], introducing new material as NLO medium can expand the domain of this area. Nowadays, a tendency to use organic materials and their better nonlinear optical properties instead of inorganic materials has increased. Furthermore, organic materials could be easily tested and adjusted for more practical applications [4]. Recently, they have been used in optical and optoelectronics devices, functioning as light emitters, second harmonic generators, frequency converters, waveguide switches, photomechanical systems, micropatterning, etc. [4]-[6]. Additionally, organic polymeric materials are suitable for nonlinear optical applications due to having easy modified structure, the ability of converting into thin films, high laser damage threshold, faster response time and other improved properties [5]. Polyurethanes are a broad class of organic materials utilized in a wide variety of applications that can be useful for nonlinear optics field.

In this research, the addition of silica nanoparticles (NPs) into polyurethane close cell (PUCC) matrix was investigated by optical microscopy, SEM imaging and Raman spectroscopy. Furthermore, the third-order nonlinear optical properties of PUCC/SiO₂ nanocomposites was obtained by using the closed- aperture (CA) and open-aperture (OA) Z-scan techniques with a Nd:YAG laser at a 532 nm with continuous-wave (CW).

II. EXPERIMENTAL

A. Materials

Silicon oxide NPs (99.5+%, S-type, spherical particles, 15–20 nm, amorphous) was prepared from US Research Nanomaterials, Inc. N, N-Dimethylformamide (DMF) and Diphenyl methane disocyanate (MDI, ρ=1.23 g/cm³) from Merck Co. Ltd. of Germany, polyether polyl (Rigid Close Cell-RCC, ρ =1.1 g/cm³) and blowing agent (HCF–C), surfactant and catalyst were prepared from Exxon Panah Co., Ltd., Tehran, Iran.
B. Preparation of PUCC/SiO$_2$
First of all, the different amount of silica was dissolved into closed cell polyol part by using an electrical MS2 Minishaker IKA (Germany). This stage lasted for 20 seconds with 3000 rpm until a homogenized solution was reached. Then the MDI part was added to the prepared solution by vortex mixing with 2000 rpm for 4–5 seconds. Due to well-prepared sample and producing CO$_2$ gas during reaction time, the cover of the container of PUCC/SiO$_2$ was taken off. After 10–12 seconds reaction was completed by forming of foams with the equal ratio of polyol:MDI. For characterization purposes, thin pieces of samples with 1 mm diameter were cut and soaked up into liquid nitrogen for preparing freezing samples.

C. Characterization
Optical micrographs were taken using an optical microscope (Nikon; TE 2000-S) in transmission mode with ×40 magnification. For evaluating possible interaction between SiO$_2$ NPs and PUCC foams, a Thermo Nicolet Almega dispersive micro-Raman scattering spectrometer with a 532 nm wavelength as the second harmonic of a Nd:YAG laser was used. The experimental Z-scan set-up of the proposed technique is shown in Fig. 1. For this method, the Nd:YAG laser beam with CW operating at 532 nm was used. According to typical preparation for this method, PUCC/SiO$_2$ nanocomposite has been dissolved into DMF until a solution with 0.1 M was achieved. The sample is moved along the z axis in the vicinity of the focal plane of 5 cm focal length lens (the +z direction is the laser propagation direction). The transmitted intensity is collected and recorded by a detector.

III. RESULTS AND DISCUSSION

A. Microscopic Evaluation
The cell size of PUCC can be estimated by optical microscopy. For this aim, thin layers of pure PUCC and PUCC nanocomposite with thicknesses of about 1 mm were cut perpendicular to the foams rising direction. The liquid nitrogen was used for freeze–fractured surfaces of all samples and after that they were examined.

![Fig. 1. Experimental set-up for the Z-scan technique.](image)

![Fig. 2. Optical micrographs of: (a) blank PUCC, (b) PUCC/1.0 wt.% and (c) PUCC/2.0 wt.% SiO$_2$.](image)

B. SEM Analysis
The exact micro structural features of the synthesized samples were characterized by image analysis of foam’s sections. The synthesized samples are analyzed under a SEM Seron Technology-AIS2100 model using 30 kV accelerating voltage after coating the samples with a thin layer of gold. All foam pictures are taken perpendicular to the foam rising direction.

By focusing on SEM images, the given results from optical micrographs are confirmed. The cell sizes were determined more exactly rather than optical imaging. It is clear in Fig. 3 that by adding SiO$_2$ NPs from 0.0 wt.% to 2.0 wt.% into PUCC, the average cell size is coarser.
Resulting samples are analyzed under a SEM in different magnifications. Here, only the SEM images of nanocomposite foams with SiO2 NPs contents of 1.0 wt.% are shown in Fig. 4. As it is seen in Figs. 4(a)–4(f), close inspection (with ×150, ×500, ×1.5k, ×6k, ×10k and ×25k magnifications, respectively) of the cell struts reveals that the PUCC/SiO2 nanocomposite foams have micro-porous skeleton. The presence of the micro voids can be explained in terms of the chemical reactivity of SiO2 NPs with the isocyanate monomer [7]. Presence of SiO2 NPs in a micro void of PUCC/SiO2 nanocomposite foams gives evidence of the mentioned claim. As a whole, the existence of micro voids can be attributed to CO2 gas generation caused by the reaction between silica-polyol groups with isocyanate groups. As this reaction is thought to occur at the silica surface on the nanoscale, the gas production leads to micro voids in the cell struts of the foam. The interfacial reaction of silica-polyol and isocyanate groups can produce micro voids in the cell struts of the foam skeleton which facilitate gas diffusion from the bulk towards the macroscopic cells.

Fig. 2 shows the transmitting optical microscopy images for PUCC and SiO2 NPs. Accordingly, by increasing of SiO2 NPs in pure PUCC the mean cell sizes in the matrix have been decreased in comparison with pure PUCC. This finding is reasonable because silica can fill the empty spaces and bring the cells close together.

![Fig. 2](image-url)

Fig. 3. SEM images of the PUCC foams with (a) 0.0 wt.%, (b) 1.0 wt.%, (c) 2.0 wt.% SiO2 NPs.

![Fig. 3](image-url)

Fig. 4. SEM images of PUCC nanocomposite loaded with 1.0 wt.% SiO2 NPs with different magnification, (a) ×150, (b) ×500, (c) ×1.5k to show micro voids, (d) ×6k, (e) ×10k, and (f) ×25k to show the cross section of cell strut.

![Fig. 4](image-url)

Fig. 5. Raman spectra of blank polyurethane and PUCC/SiO2 nanocomposite foams with different loading fractions of SiO2 NPs in the Raman shift region of 450–1650 cm$^{-1}$.

**C. Raman Spectra of PUCC/SiO2**

The Raman spectra of the synthesized samples (Fig. 5) are used for evaluating possible interaction between SiO2 NPs and PUCC foams. It can be seen that by adding SiO2 NPs in PUCC matrix the C–H wagging bond at 850 cm$^{-1}$ has been appeared stronger [8]. This peak
was shifted toward lower wave numbers by increasing the amount of SiO₂ NPs in PUCC matrix. The Raman peaks at 626 cm⁻¹ [8], 760 cm⁻¹ [9] and 1045 cm⁻¹ [10] are assigned as the C–C–C bending mode, Si–O bending and Si–O–Si stretching vibration bond, respectively, that are just in PUCC/SiO₂ samples but more SiO₂ into PUCC matrix causes more shift toward higher wave numbers. All the synthesized samples have C–C stretching bond at around 1590 cm⁻¹ [8] and by adding SiO₂ NPs to pure PUCC the intensity of this peak starts to increase.

D. Nonlinearity Capability

1) Z-scan theories on nonlinear process

The Z-scan technique is a very important single beam method for measuring the nonlinearity of optical materials. The Z-scan method has two experimental set-ups, with a small aperture (CA) and without any aperture (OA), in order to determine \( n_2 \), the nonlinear refractive (NLR) index, and \( \beta \), nonlinear absorption (NLA) coefficient, respectively [11]. In CA Z-scan measurements, an aperture is placed in front of the detector to prevent some of the light from reaching the detector. However, in OA measurements, aperture was replaced by a lens to collect all the light into the power meter of the detector [12].

The ordinary relation for NLR index is
\[
n(I) = n_0 + n_2 I \quad \text{[13]}
\]
where \( n(I) \) is the total refractive index, \( n_0 \) the linear refractive index, \( n_2 \) the NLR index and \( I_0 = 2P_{in} / \pi \alpha_0^2 \) [14] is the incident intensity at focal point that is 2493.7 W/cm² and \( P_{in} \) is the laser power that is 55 mW in this work. Also the radius of the waist of the illumination beam inside the sample as \( \alpha_0 \) is determined equal to 37 µm. The Rayleigh diffraction length is 8.1 mm at the focal plane.

At low incident powers, the linear absorption was evaluated by following Eq. 1 [11], [14] that \( P \) and \( P_0 \) are referred to output power with and without sample, respectively.

\[
\alpha = -\frac{1}{L} \ln \left( \frac{P}{P_0} \right) \quad \text{(1)}
\]

A phase shift occurs by an optical beam travelling a distance \( L \) in the medium with the following relation [13]:

\[
|\Delta \varphi_0| = -\left( \frac{2\pi}{\lambda} \right) \Delta n L_{eff} \quad \text{(2)}
\]

where the \( L_{eff} \) is an effective sample thickness, \( L_{eff} = \left( 1 - e^{-a \ell} \right) / \alpha \), and \( \Delta n \) is related to NLR index [13]. The equivalent relation for Eq. 2 is:

\[
|\Delta \varphi_0| = \left( \frac{2\pi}{\lambda} \right) n_2 I_0 L_{eff} \quad \text{(3)}
\]

By using CA scheme, the value of distance between the normalized transmitted peak and transmitted valley is nominated by \( \Delta \varphi_0 \) that it was related to \( |\Delta \varphi_0| \) with the following expression [13]:

\[
\Delta T_{p-v} = f |\Delta \varphi_0| \quad \text{for} \quad \Delta \varphi_0 < \pi \quad \text{(4)}
\]

The \( f \) factor is an experimental constant and is assigned by means of a parameter, \( S \), as the aperture’s linear transmission, that is 0.3 (or 1) for closed (or open) aperture Z-scan experiment. The following equation \( f = 0.406(1 - S)^{0.25} \) can be evaluated this factor and then by putting the amount of \( f \) into Eq. 4, the NLR index; \( n_2 \left( \text{cm}^2/\text{W} \right) \) can be obtained from following equation [13, 15]:

\[
\Delta T_{p-v} = 0.406(1 - S)^{0.25} \left( \frac{2\pi}{\lambda} \right) n_2 I_0 L_{eff} \quad \text{(5)}
\]

The nonlinear behavior of the sample is equivalent to the formation of an induced positive or negative lens as self-focusing (positive) or self-defocusing (negative) nonlinearity [4], [11-14]. Experimental results of Z-scan data with an aperture is divided by those without an aperture to obtain pure nonlinear refraction.
The other parameter which can be determined from the OA Z-scan technique experiment is the NLA coefficient $\beta$. The absorption coefficient is assigned as $\alpha(I) = \alpha_0 + \beta I$ that $\alpha_0$ is the linear absorption coefficient and is calculated by Eq. (1) and $I$ is the intensity of the incident laser light [11]. In combination with the known NLA coefficient, for induced absorption $\beta>0$ and for induced transparency or saturation of linear absorption $\beta<0$ [16-17]. The amount of $\beta$ is estimated by fitting the OA Z-scan trace with the following equations [15]:

$$T_{\text{norm}}(z) = \frac{\ln(1+q_0(z,t))/q_0(z,t)}{L}$$

(6)

$$q_0(z,t) = \beta I_0 L_{\text{eff}}/(1+z^2/z_0^2)$$

(7)

That $z_0 = k \omega_0^2/2$ is the diffraction length of the beam and $k = 2\pi/\lambda$ is the wave vector. It is seen that the OA transmittance is symmetric with respect to the focus ($z=0$), where it has a minimum transmittance value.

2) CA Z-scan results

The laser source used in Z-scan experiment is a frequency-doubled Nd:YAG laser operating at 532 nm. The spatial profile of the beam is of Gaussian distribution with TEM$_{00}$ mode. The beam is focused by a 50 mm focal length lens to produce a focused beam with the beam waist radius ($\omega_0$) of about 37 $\mu$m at the focal plane. The sample was placed in a 1 mm thick quartz cell. The sample could be moved along the beam path and about the focal plane of the lens.

The linear absorption, $\alpha$, was calculated by using Eq.1 for low power. The values of $\alpha$ for different concentrations of silica in PUCC are listed in Table 1.

Both of the NLA and NLR parameters have important role in the CA Z-scan [18]. So, for getting the CA curve, the CA data must be divided by the OA data to eliminate the contribution of NLA. The CA ($S=0.32$) scheme allowed to determine both of the sign and the magnitude of $n_2$. Fig. 6 shows pure closed Z-scan data of different compositional percentages of SiO$_2$ NPs in blank PUCC.

In Table 1 the values of $n_2$ for different compositional percentages of SiO$_2$ NPs in PUCC were demonstrated. The curve of the normalized transmittance that presents a peak followed by a deep valley indicates the negative sign for NLR index which can be identified as a self-defocusing effect of the synthesized samples. The NLR indices coefficients of the synthesized samples were obtained from Eq. (5) in the order of $10^{-8}$ (cm$^2$/W).

![Fig. 6. Closed aperture of Z-scan experimental curves of blank PUCC and PUCC/SiO$_2$ nanocomposites.](image-url)
NPs from 0.0 wt.% to 2.0 wt.% into polymer matrix, the amount of NLR has increased.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔT</th>
<th>α (cm⁻¹)</th>
<th>L₀eff (mm)</th>
<th>n² × 10⁻⁵ (cm²/W )</th>
<th>β (cm/W ) × 10⁻⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PUCC</td>
<td>0.019</td>
<td>0.666</td>
<td>0.967</td>
<td>0.176</td>
<td>8.27</td>
</tr>
<tr>
<td>PUCC/1% SiO₂</td>
<td>0.043</td>
<td>0.675</td>
<td>0.967</td>
<td>0.405</td>
<td>12.4</td>
</tr>
<tr>
<td>PUCC/2% SiO₂</td>
<td>0.061</td>
<td>0.710</td>
<td>0.965</td>
<td>0.571</td>
<td>30</td>
</tr>
</tbody>
</table>

3) OA Z-scan results

In the case of the OA Z-scan, the transmittance is a function of nonlinear absorbance in the sample [21]. Magnitude and sign of NLA coefficient of the samples was determined through OA Z-scan. It is seen that the OA transmittance is symmetric with respect to the focus, (z=0) where has a minimum transmittance. Fig. 7 shows the OA Z-scan curves obtained for PUCC/SiO₂ nanocomposites.

It is obvious that the OA and CA curves of the pure sample are much lower than the other curves in Figs. 6 and 7. In the PUCC/SiO₂ nanocomposites, the contribution of blank PUCC to the nonlinearity is less than PUCC/SiO₂ NPs. Following other researches, the nonlinear response of the synthesized samples is related to the presence of two photon absorption (TPA) effect [2], [16].

There have been few reports for the investigation of NLO properties of PU nanocomposites. Wang et al. measured a self-defocusing refraction effect with the NLA coefficient and the NLR coefficient are 

$$n = -53 \times 10^{-9} \text{ cm/W }$$

and

$$\beta = -2.8 \times 10^{-12} \text{ cm }^2 \text{ W}^{-1},$$

for the 0.6% PU/MWNT film sample which is excited by the nanosecond laser pulse (pulse duration of 8 ns) at 532 nm, respectively [22]. It is clear that both of the NLR and NLA for PU/MWNT are smaller than the corresponding values for PU/SiO₂ nanocomposites.

By adding silica to PUCC, the polarity of system was increased. This is a main factor for rising NLO response of system [13], [15]. Considering our results in nonlinear optics filed, silica can increase nonlinear absorption and refraction index of the system.

By controlling the optimum ratio of silica into PUCC, the PUCC/SiO₂ nanocomposites can be suggested as a promising and helpful candidate for applications in real optical systems. Thus, PUCC/SiO₂ nanocomposite with larger nonlinear coefficients is a promising nonlinear material, and its nonlinear coefficients can be adjusted.

IV. CONCLUSION

PUCC/SiO₂ nanocomposite has been prepared by using in situ polymerization approach. The
third-order optical nonlinearities of PUCC/SiO$_2$ nanocomposites, dissolved in DMF are characterized by Z-scan technique with CW Nd:YAG laser at its second harmonic frequency of 532 nm as a source light. The new compound exhibit good optical limiting properties at the wavelength used. The results conclude that it is promising candidate for the future optical device applications. The Raman spectra of the synthesized samples are used for analyzing possible interaction between SiO$_2$ NPs and PUCC foams. The other following points which can be concluded:

- By increasing SiO$_2$ NPs contents into PUCC matrix, the mean cell sizes of the synthesized samples are decreased.

- The NLR index of the samples was obtained from CA Z-scan in the order of $10^{-8}$ (cm$^2$/W) with negative sign. By adding SiO$_2$ NPs into blank PUCC the NLR index increased.

- The NLA coefficients of the samples were obtained from OA Z-scan in the order of $10^{-5}$ (cm/W) with negative sign. By adding SiO$_2$ NPs into blank PUCC, the amount of $\beta$ is increased that may be mainly attributed to TPA effect.

**REFERENCES**


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