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Research Article

Gas Flow Rate Effect on the Nonlinear Optical Properties of Ag/Pmma Nanocomposite Thin Films Prepared by Aerosol Assisted Dielectric Barrier Discharge Plasma Jet Polymerization

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Abstract

Silver PMMA Nanocomposite Thin Films Deposited on Glass Substrates by in-situ aerosol assisted plasma jet polymerization at atmospheric pressure and room temperature, from MMA monomer in the presence of 7wt% concentrations of Ag nanoparticles. The effects of argon gas flow rate on the linear and nonlinear optical properties of Ag/PMMA nanocomposite films are studied. It is shown that the changed in gas flow rate does not affect the linear properties while the nonlinear properties have an arbitrary changes with gas flow rate increase. The prepared thin films are characterized by UV-Visible, XRD, FT-IR, AFM, the nonlinear optical properties are measured by Z-scan technique using second harmonic of pulsed Nd:YAG laser 532nm and pulse duration of 30ns, the third order nonlinearity are determined the nonlinear refractive index n_2, nonlinear absorption coefficient β, as well as the real and imaginary parts of third order susceptibility X^3 all are changed due to effect of plasma and gas flow rate.

Keywords: *PMMA, nonlinear optical properties, plasma polymerization, nanocomposite.*

1. Introduction

Materials with large third-order optical nonlinearities and fast time response are essential for potential applications in optical signal processing, high-speed all optical switches, optical bistability, optical limiting (OL) and so on (Hong Shen *et al*, 2006, Elizabeth, 2010). Metal nanocomposites have attracted much attention due to their distinctive chemical and physical properties. Silver nanoparticles have garnered much attention these days due to numerous application areas stemming from local field enhancement effects near the surface plasmon resonance frequency (Noorsaiyyidah *et al*, 2014, Saima *et al*, 2012). Silver (Ag) nanoparticles are particularly important due to their high electrical and thermal conductivities and exhibit strong absorption of electromagnetic waves in the visible range due to surface plasmon resonance (SPR). SPR is caused by collective oscillations of the conduction electrons of nanoparticles upon irradiation with visible light. The SPR is highly influenced by the shape and size of nanoparticles (Noorsaiyyidah *et al*, 2012).

Poly methyl methacrylate (PMMA) is well known as a polymeric glass and engineering plastic with a wide range of applications it is a hard, rigid and having a high transparency and a relatively low glass-transition temperature (Vodnik *et al*, 2009, Mohammed *et al* 2011).

Plasma polymerization plays a significant role due to its cost effectiveness and simplicity, and it's also offer good quality, pinhole free and homogeneous films and can be defined as the formation of polymeric materials under the influence of plasma (Sajeev, 2006, Menno, 2000). Earlier work on the nonlinear optical properties of Ag/PMMA nanocomposite polymer film by Yang Deng *et al* (Yan Deng *et al*, 2006), the nanocomposite films were prepared by a simple in situ synthesis, the nonlinear optical properties were measured by Z-scan technique with 13ns pulse duration and 532nm, the nonlinear refractive index and nonlinear absorption coefficient were measured to be 5.781×10^{-2} cm^2/GW and 2.225×10^{3} cm/GW, respectively and later many research were done on the other polymeric material like PVA by Faraji *et al* (Faraji *et al*, 2012).

In present work, we used a dielectric barrier discharge plasma jet system for the deposition of Ag/PMMA nanocomposite films with silver nanoparticles concentration of 7wt% and three different condition for argon gas flow rate, these films were characterized by UV-Vis, AFM, XRD, FT-IR and compared with pure PMMA films deposited at the same conditions, and the nonlinear optical properties were studied by using Z-scan technique.

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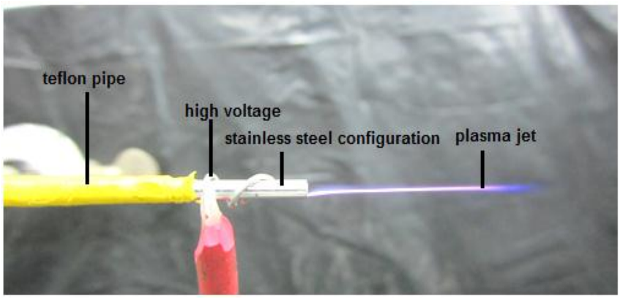


Figure (1): Photograph at working of the non-thermal atmospheric pressure plasma torch

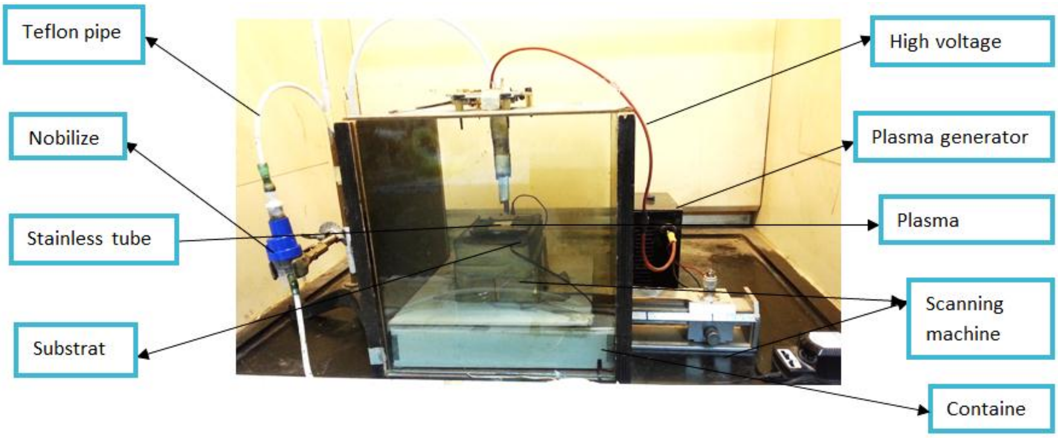


Figure (2): Photograph for the non-equilibrium atmospheric pressure plasma system for Silver/PMMA nanocomposite thin films preparations

2. Experimental details

The Dielectric Barrier Discharge (DBD) plasma jet system used for the films deposition consist of alternating high voltage power supply, generates high voltage of sinusoidal shape of 7.5 kV peak to peak and fixed frequency of 28 kHz, plasma jet torch, gas supply and fitting. Figure (1) shows a photograph at working of the non-thermal atmospheric pressure plasma torch.

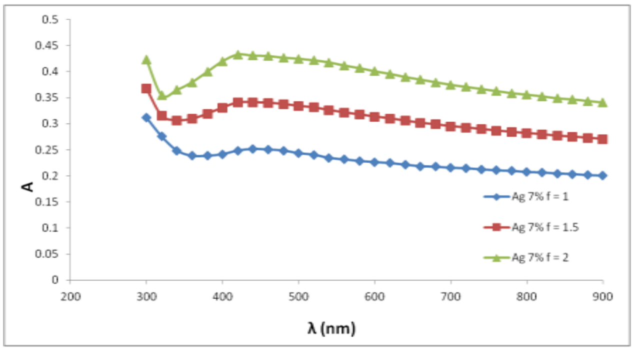
Silver nanoparticles from Nanjing nano Technology co, ltd, China its particle size was 50nm and purity of 99.9%, with concentration of 7wt% was mixed with Methyl Methacrylate Monomer (MMA) product from Vertex-Dental Netherlands. The mixer dispersed by ultrasonic to ensure a homogeneous distribution of nanoparticles. Then silver PMMA nanocomposite thin films deposited by DBD plasma jet system on ultrasonically cleaned glass substrate of standard size 10 x 10 mm. Figure (2) shows a photografe for the non-equilibrium atmospheric pressure plasma system for Silver/PMMA nanocomposite thin films preparations. When the Argon gas passes through the nobilizer which contains the mixture, the mixture convert to aerosol. This aerosol was guided by the Ar gas to the plasma jet. The plasma was ignited by using an electric source at a fixed frequency of 28 kHz. The plasma was generated downstream to the substrate which was positioned along the plasma jet at a fixed distance from the plasma torch (1.5cm). The film deposition was carried out for 5min.Three levels of gas flow rate (1, 1.5, and 2 L/min.) were used in this work.

UV-Visible absorption spectra of pure PMMA and Ag/PMMA nanocomposite thin films were obtained by using a double beam UV-Vis-NIR 210A Spectrophotometer. (FT-IR) type 8000 series Fourier transform product of Shimadzu Company was employed to investigate the chemical structure of these nanocomposite thin films. The thin films surface morphological analysis is carried out by employing an Atomic Force Microscope(AFM) type (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS) from Angstrom Ad-Vance Inc, and the structure analysis are achieved by X-ray diffractometer system type SHIMADZU 6000. The thickness of the films was measured by optical interferometric method. The nonlinear optical properties were measured by Z-scan technique with open and close aperture using pulse second harmonic Nd:YAG laser of wavelength 532nm and pulse duration of 30 ns finally collimated lens of focal length 10 cm, input energy 30mJ, the transmitted energy were monitored by the optical detector type (DPSS 1830C).

3. Results and discussion

A. Linear optical properties

Figure (3) shows the absorbance (A) spectra of Ag/PMMA nanocomposite thin films and pure PMMA thin films and table (1) shows the thin films preparation conditions and its thickness. The absorption spectra of Ag/PMMA films shows the effect of Ag nanoparticles and the enhancement of SPR which is represented by the peak at 420nm while pure PMMA films have absorption peak at 294nm and transparent from 300 to 900nm.



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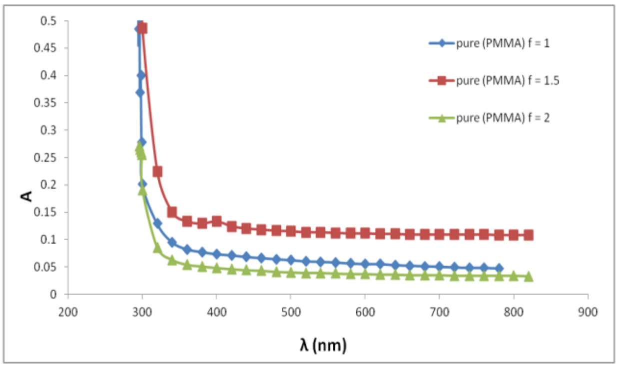


Figure (3): (a) Absorption spectra for Ag/PMMA nanocomposite thin films for 7wt% Ag concentration, (b) For pure PMMA thin films for different gas flow rate

Table (1): Thin films preparation conditions and its thickness

Samples code	Description	Thickness(nm)	Gas flow rate (l/min.)
P1	Pure PMMA	275	1
P2	Pure PMMA	329	1.5
P3	Pure PMMA	213	2
Ag4	PMMA+7%Ag	311	1
Ag5	PMMA+7%Ag	259	1.5
Ag6	PMMA+7%Ag	282	2

Figure (4) shows the optical energy band gap for Ag/PMMA at different gas flow rate. The optical energy band gap has been determined by plotting the variation of $(\alpha h\nu)^2$ versus $h\nu$ (eV) where the Eg for PMMA direct energy gap transition. The increasing gas flow rate from (1 to 2 L/min) was lead to increase the energy band gap E_g from 2.51 to 2.86 eV. Figure (5) shows the optical energy band gap for pure PMMA at different gas flow rate. The energy band gap is increasing from 4.05 to 4.11 eV when the gas flow rate increases from 1 to 2 L/min.

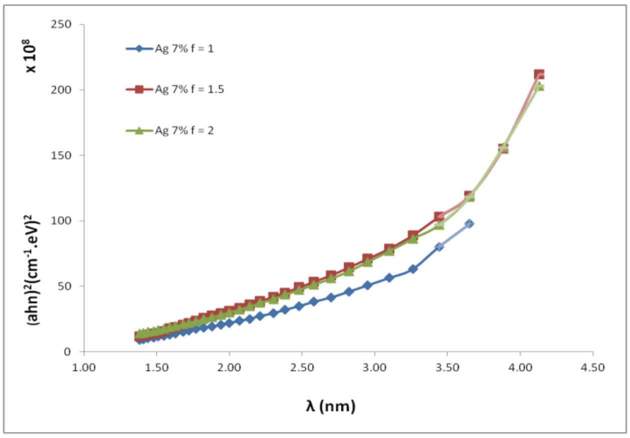


Figure (4): The effect of gas flow rate on the optical energy band gap for Ag/PMMA nanocomposite thin films

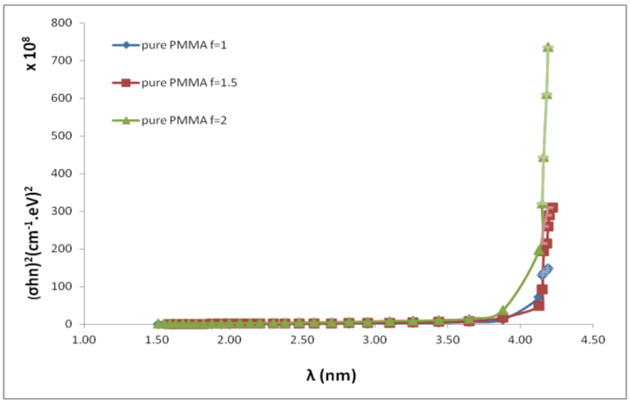


Figure (5): The effect of gas flow rate on the optical energy band gap for PMMA thin films

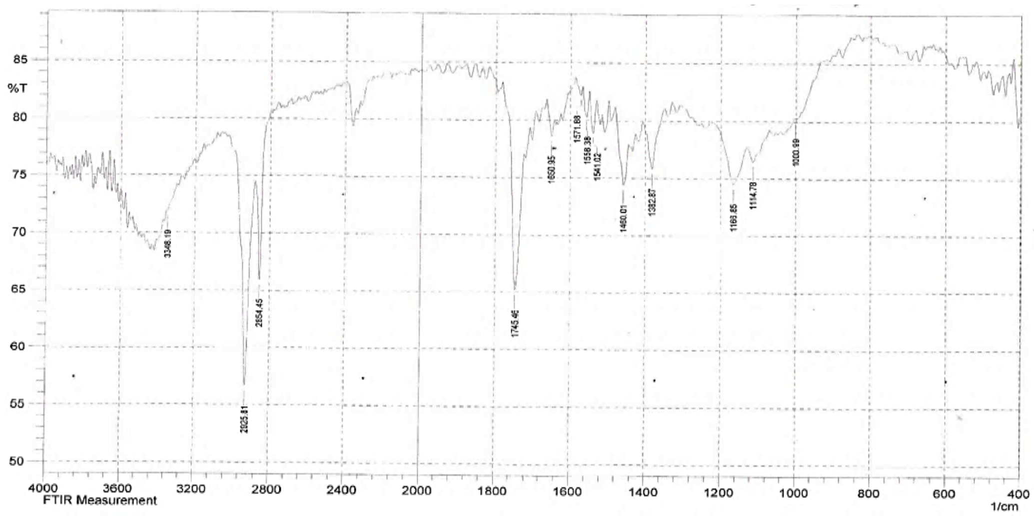
B. FT-IR analysis

Figure (6) shows the FT-IR spectra for pure PMMA and Ag/PMMA nanocomposite thin films. The FT-IR absorption bands for pure PMMA and Ag/PMMA nanocomposite thin films are given in table (2).

The FT-IR spectrum of PMMA indicates the details of functional groups presents in the synthesized PMMA and these results agree with (Tota, 2007, Mas Rosemal *et al*, 2010), it can also see a shift in C=O ester carbonyl group, C=C, CH_3, C-C for the Ag/PMMA nanocomposite thin films this indicates that the silver nanoparticles modify the PMMA thin films structure.

Table (2): FT-IR absorption bands for PMMA and Ag/PMMA nanocomposite thin films

Bond range(cm^{-1})	PMMA	Ag/PMMA	Expected vibration
(2850-2950)	2854.45 2925.81	--	C-H
(1720-1740)	1745.46	1739.67	C=O ester carbonyl group stretching vibration
Around 1630	1650.95	1647.1	C=C
(1395-1450)	1460.01	1396.37 1450.37	CH_3
Around 1388	1382.87	--	$O\text{-}CH_3$
(1150-1250)	116.85	--	C-O-C stretching of ester group
(1050-1300)	114.78 1166.85	--	C-O
(700-1300)	1000.99	750 1072.35	C-C
		694.33,568.96 507.24,449.38 418.52	Ag



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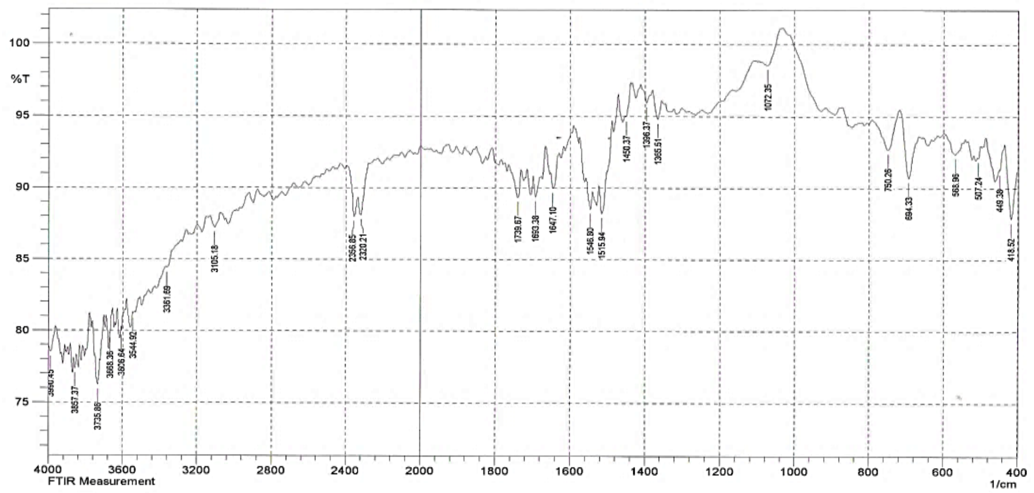


(b)

Figure (6): FT-IR spectrum (a) for PMMA (b) for Ag/PMMA nanocomposite

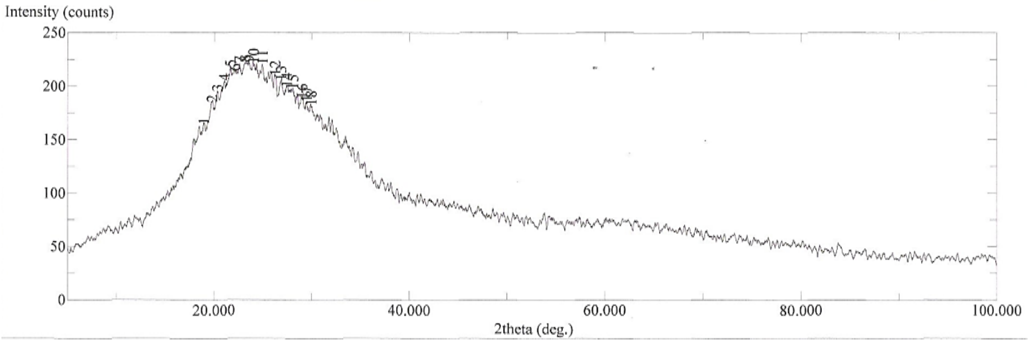


Figure (7): XRD for pure PMMA thin film

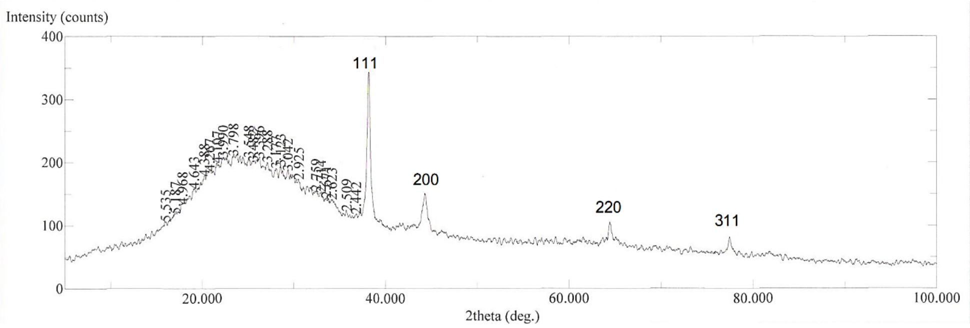


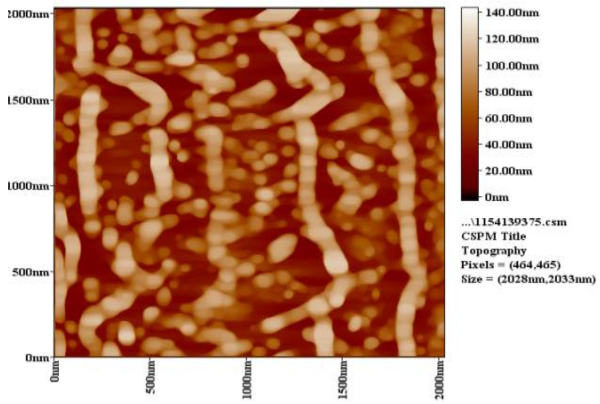
Figure (8): XRD for Ag/PMMA nanocomposite thin film

C. XRD

Figure (7) shows the XRD pattern of the prepared pure PMMA thin film and Figure 8 for Ag/PMMA nanocomposite thin films, for pure PMMA the film has an amorphous structure. The XRD pattern of Ag nanoparticles in PMMA, All the refractions corresponded to the pure silver metal with cubic symmetry. The refractions presented by four main peaks at 2θ= 38.160, 44.320, 64.440 and77.40◦which are assigned to the lattice planes (1 1 1), (2 0 0), (2 2 0), and (3 1 1) this agree with (Noorsaiyyidah *et al*, 2012, Nastaran *et al*, 2014).

D. Surface morphology

The surface morphology of the pure PMMA and 7wt% Ag/PMMA nanocomposite thin films were examined by AFM. The surface roughness of plasma polymerized pure PMMA thin films 23A°and for 7wt% Ag/PMMA thin films was 5Å. The low surface roughness of plasma polymerized silver PMMA composite confirms that the technique of plasma polymerization can be employed to produce extremely smooth films with very small surface roughness when compared to films prepared by other techniques. It is clear that the silver nanoparticles are uniformly distributed within the scanning area. Figure (9a and b) represent the 3-D and 2-D AFM photos of the pure PMMA thin films surface and c shows the granularity distribution chart. The average diameters of clusters are 90.85nm. Figure (10 a and b) represent the 3-D and 2-D AFM photos of the 7wt% silver /PMMA thin films surface and c shows the granularity distribution chart. The average diameter of clusters was 86.88nm. The addition of silver nanoparticles reduce the surface roughness of the nanocomposite thin films and this gives an indication that silver nanoparticles are uniformly distributed within scanning area.



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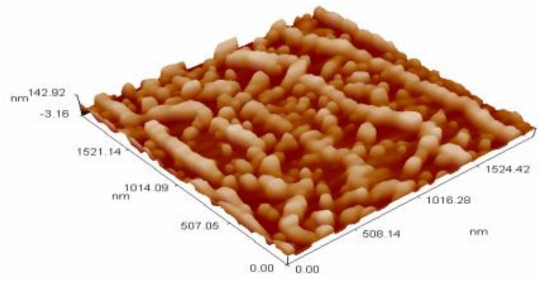

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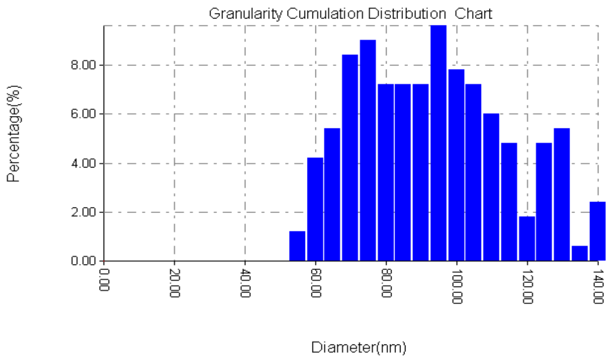
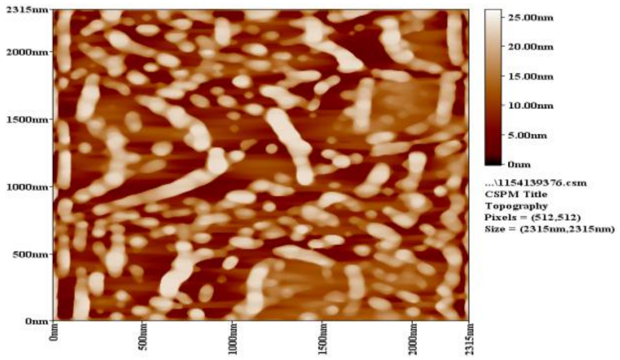


(c)

Figure (9): AFM photographs of PMMA film surface (a) 2D view,(b) 3D view, (c) the granularity distribution chart



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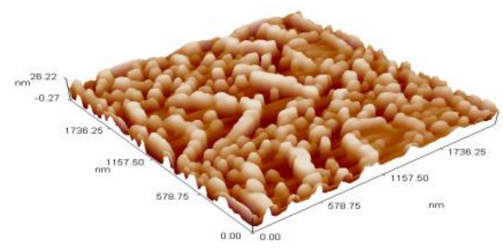

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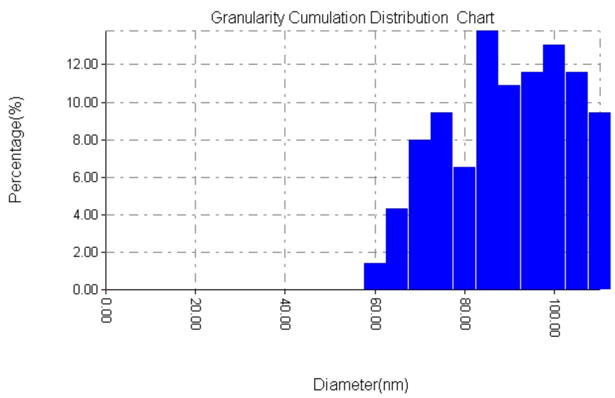
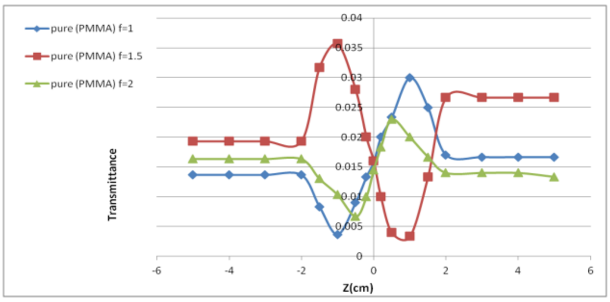


Figure 10): AFM photographs of 7wt% silver PMMA nanocomposite film surface (a) 2D view,(b) 3D view, (c) the granularity distribution chart

E. Nonlinear optical properties

In this part we present the nonlinear optical properties, the nonlinear refraction, nonlinear absorption in the term of nonlinear refractive index n_2 and nonlinear absorption coefficient β. The Z-scan curves for close and open aperture for pure PMMA thin films prepared with three different gas flow rate are represented in figure (11) and for Ag/PMMA nanocomposite thin films represented in figure (12). The values of n_2, β are calculated according to Z-scan theory and real and imaginary parts of the third order nonlinear susceptibility X^3[11] as listed in the table 3, from this table we can see the changes in the nonlinearity of the samples this is according to the effect of plasma during the deposition and also the effect of gas flow rate. The importance parameters that affect the plasma polymerization process are; namely, flow rate (F), power (W) and the molecular weight of the precursor (M). All three parameters have been shown to be important in the description and control of experimental conditions of the plasma polymerization process. Most emphasis has been on the effect of W, F and M on rates of deposition and, to lesser extent, chemical composition (Ashok and Yasuda, 1983). In our work M and W are fixed so the monomer flow rate is the dominant factor and effected polymer chemical composition and then on non-liner optical properties, and we can see this changes clearly from the changes of major peaks of FT-IR spectrum of the samples this agree with (Davoud *et al*, 2012).



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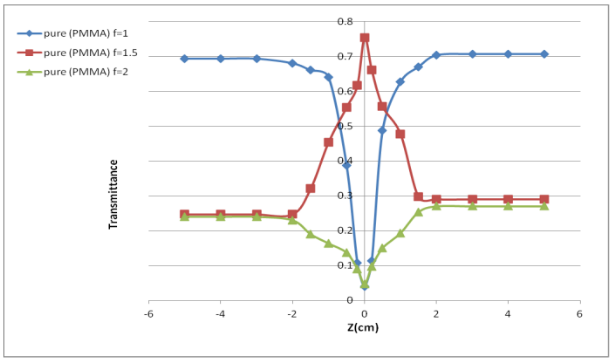
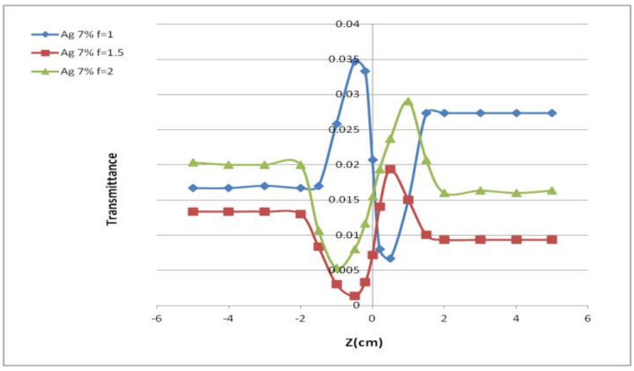


(b)

Figure (11): Z-scan curves for pure PMMA films (a) close aperture. (b) open aperture

Table (3): Values of n_2, β and X^3

Samples code	n_2 *10^{-2} (cm^2/GW)	β*10^3 (cm/GW)	Re X^3	Im X^3	X^3
P1	2.612	2.706	2.09*10^{-10}	0.916	0.9159
P2	2.855	17.398	3.65*10^{-10}	9.41	9.4095
P3	2.044	3.746	1.3*10^{-10}	1.01	1.00917
Ag4	3.335	17.452	1.05*10^{-9}	23.3	23.3386
Ag5	2.532	2.724	1.48*10^{-9}	6.76	6.7639
Ag6	3.334	27.252	3.74*10^{-9}	129	129.0572



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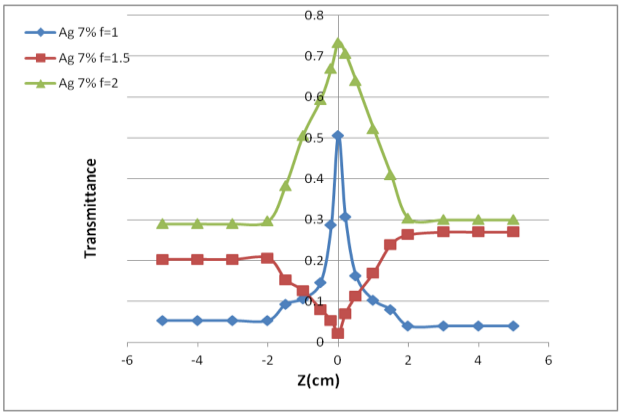

(b)

Figure (12): Z-scan curves for Ag/PMMA nanocomposite films (a) close aperture. (b) Open aperture

Conclusions

As is clear, the preparation of nanocomposite films by plasma polymerization made a new material with different chemical structure, plasma polymerized polymer different from conventional polymer that it has high cross linked, highly branched and high density and this effect on the linear refractive index so the nonlinear properties are also affected. In our case the change in flow of argon gas made dramatic changes in the nonlinear optical properties, the n_2, β and third order nonlinear susceptibility while the linear parameters of this polymer are kept unchanged. These observed results can be explained by the change in chemical structure and chemical bonds that occurred due to the effect of plasma as well as the gas flow.

References

Ashok K. Sharma, H. Yasuda (1983), Plasma polymerization of tetramethyldisiloxane by a magnetron glow discharge, thin solid films, vol.110, pp.171-184.

Davoud Dorranian, Yasaman Golian and Alireza Hojabri (2012),Investigation of nitrogen plasma effect on the nonlinear optical properties of PMMA, Journal of Theoretical and Applied Physics, vol.6, pp.1-8.

Elizabeth C V (2010), nonlinear optical properties of organic and polymer Systems: theoretical and experimental investigation, Cochin University of Science and Technology, KOCHI-22, India

Faraji N., W. Mahmood Mat Yunus, A. Kharazmi, E. Saion, M. Shahmiri, N. Tamchek (2012), Synthesis, characterization and nonlinear optical properties of silver/PVA nanocomposites, J. Europ. Opt. Soc Rap. Public., vol.7, pp.12040-1-12040-7.

Hong Shen, B L Cheng, G W Lu, D Y Guan, Z H Chen and G Z Yang (2006), Picosecond nonlinear optical responses of Au/PVP composite films, J. Phys. D: Appl. Phys., vol. 39, pp.233–236.

Mas Rosemal H. Mas Haris, S. Kathiresan, S. Mohan (2010), FT-IR and FT-Raman Spectra and Normal Coordinate Analysis of Poly methyl methacrylate, Scholars Research Library, Der Pharma Chemica, Vol.2, pp. 316-323.

Menno Thomas van (2000), Surface Modification by Plasma Polymerization: Film Deposition, Tailoring of Surface Properties and Biocompatibility, University of Twente, Enschede, The Netherlands, Ph.D Thesis.

Mohammed Alsawafta , Simona Badilescu , Abhilash Paneri (2011), Vo-Van Truong and Muthukumaram Packirisamy, Gold-Poly(methyl methacrylate) Nanocomposite Films for Plasmonic Biosensing Applications, Polymers,vol.3.

Nastaran Faraji, W. Mahmood Mat Yunus, Alireza Kharazmi, Elias Saion (2014), Third-order nonlinear optical properties of silver nanoparticles mediated by chitosan, Optic, pp.1-4.

Noorsaiyyidah Darman Singho, Mohd Rafie Johan and Nurul Akmal Che Lah (2014), Temperature-dependent properties of silver-poly (methylmethacrylate) nanocomposites synthesized by in-situ technique, Nanoscale Research Letters, vol.9, pp.1-6.

Noorsaiyyidah Darman Singho, Nurul Akmal Che Lah, Mohd Rafie Johan, Roslina Ahmad (2012), FTIR Studies on Silver- Poly (Methylmethacrylate) Nanocomposites via *In-Situ* Polymerization Technique, Int. J. Electrochem. Sci., vol.7, pp.5596-5603.

Saima Husaini, Huayu Teng, Vinod M. Menon (2012), Enhanced nonlinear Optical response of metal nanocomposite based photonic crystals, Applied Physics Letters, vol. 101, pp. 111103-1-111103-4.

Sajeev U.S (2006), Plasma polymerized organic thin films-A study on the structural, electrical and nonlinear optical properties for possible applications, Cochin University of Science and Technology Cochin-682022, India.

Tota Pirdo Kasih (2007), Development of novel potential of plasma polymerization techniques for surface modification, Gunma University, Thesis for The Degree of Doctor of Engineering.

Vodnik V.V., D.K. Božanić, E. Džunuzović, J. Vuković, J.M. Nedeljković (2009), Thermal and optical properties of silver poly(methylmethacrylate) nanocomposites prepared by in situ radical polymerization, European Polymer Journal, vol.64, pp.1-22

Yan Deng , Pei Wang , You-Yi Sun , Hai Ming , Qi-Jing Zhang, Yang Jiao, Xiao-Quan Sun (2006), Nonlinear optical properties of Ag/PMMA nanocomposite polymer film, IEEE, vol.39, No.10.