STUDY THE FLOW BEHAVIOR OF GNPS FILLED WATER AND POLYMER USING CONE-ON PALE VISCOMETER

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Abstract

This work investigates the rheological behavior of gold nanoparticles filled water (GNPS- water) and filled polyvinyl alcohol (GNPs- PVA) prepared by Nd - YAG laser ablation. Noble metal GNPs were synthesized by pulsed (Q-switched, 1064-Nd: YAG, 8 ns pulse duration and energy E=550mJ and 650mJ laser ablation of gold metal plates immersed in double distilled and deionized water DDDW and PVA solutions. Absorbance spectra of the produced nanoparticles solution was measured by UV-VIS spectrophotometer which show sharp and single peaks 530 nm indicating the produced Au nanoparticles with a narrow size ranging from 10nm to 20 nm with almost spherical shape.The morphology and size was estimated by TEM for GNPs -water .The rheological behavior of GNPs filled water with particle sizes (10 nm) and (20 nm) called nano1 and nano2 and (GNPs- PVA) called nano3 and nano4 respectively were tested using cone –on - plate viscometer.The viscosity, torque, shear stress where measured at different shear rate. The results show that the shear stress increases with the shear rate increasing for nano1, nano2, nano3 and nano4. The viscosity decreased with the shear rate increasing for nano1 , nano2 ,nano3 and nano4.The viscosity for 10 nm concentration is lower than that for 20 nm concentration due to the difference in particles size and energy value .

Keywords: GNPS- water, polyvinyl alcohol (PVA), Viscosity, Flow behavior, Shear Thinning, Cone –on - plate viscometer.

1. Introduction

Polymer Material have a great attention in resent year in Many applications in the medical filed and engineering application due to interesting properties such as lightness, toughness, cheapness and simplicity of the forming operations [1]. The gold nanoparticles (GNPs) aqueous solution exhibit particles significance in rheological behavior as non - Newtonian flow. Nanoparticle size has been shown to be an extremely important parameter affecting the nanoparticle uptake and cellular internalization. Mostly gold and silver, has attracted much interest due to their surface Plasmon resonance related properties that are potentially useful for their biological applications[2].Gold nanoparticles (Au NPs) are promising metal nanoparticles, utilized in drug delivery , bio sensing and bio labeling applications due to their unique optical and electronic properties[3,4].These properties are size and shape dependent, hence gold nanoparticles with different shapes and sizes are required for each application. In addition, the Au NPs are also having biological activities such as antioxidant, anti-inflammatory, anti-angiogenesis and anticancer properties [3]. Laser ablation in liquid environment is capable to produce metal NPs without using any surface active substances, called also as ‘‘green synthesis’’[5,6]. With this method, can be prepared NPs without chemical surfactants, therefore, having a more direct and reliable response to their surrounding material, increasing the possibility to be used in a wider range of applications [5]. Nanoparticle distribution within the body is based on various parameters such as their relatively small size resulting in longer circulation times and their ability to take advantage of tumor characteristics. For example, nanoparticles less than 20 nm in size are able to pass through blood vessel walls and such small particle size allows for intravenous injection as well as intramuscular and subcutaneous applications [7]. The rheological measurements are performed with a cone and plate geometry with a cone diameter 25 mm and a cone angle of 1°. All experiments are conducted at a constant gap of 0.5 mm and an initial stabilization period of 2 minutes is given for achieving the temperature equilibration. The liquid is placed on horizontal plate and the cone is placed into it. An electrically commutated synchronous motor drive rotates the cone at a set speed and this determines the shear rate inside the annulus of the sample. The sample tends to drag the plate, and the force it exerts on that plate (torque) is measured, which can be converted to a shear stress. Viscosity is calculated from the shear stress shear rate relation [8, 18] .Solution viscosity, as controlled by changing the polymer concentration, has been found to be one of the biggest determinants of fiber diameter and morphology when spinning polymeric Nano fibers. At low polymer concentrations, defects in the form of beads and droplets have been observed. Increasing the solution viscosity by increasing the polymer concentration yielded uniform fibers along with the formation of a few beads [8]·They found that increasing the temperature yielded fibers with decreased fiber diameter and this reduction in diameter was attributed to the decrease in the viscosity of the polymer solutions at higher temperatures, Casper *et al*· [9].The release of drug from semi-solid carriers is influenced by the rheological behavior as well. The effect of certain parameters such as storage time on the quality of GNPs can be also investigated via rheological measurements [10]. Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer (not to be confused with polyvinyl acetate, popular wood glue). It has the idealized formula $[CH_2CH\ (OH)]_n$. It is used in papermaking, textiles, and a variety of coatings. It is white (colorless) and odorless. It is sometimes supplied as beads or as solutions in water. Used in eye drops (such as artificial tears to treat dry eyes) and hard contact lens solution as a lubricant .As a surfactant for the formation of polymer encapsulated Nano beads .Used in protective chemical-resistant gloves, as an embolization agent in medical procedures. Carotid phantoms for use as synthetic vessels in Doppler flow testing .Structure and properties. PVA is close to incompressible. The Poisson's ratio is between 0.42 and 0.48. PVA is nontoxic it biodegrades only slowly [11,12] . Mixing is generally considered as a complex subject, but its essence is quit simple: related stretching and folding of fluid elements [15, 16]. Nanofluids preparing by Laser ablation method is safe, easy, and gives homogenous distribution nanofluid in one step. This method can be defined as the process of liberating particles from a solid surface by irradiating it with a laser beam [16].

The objective of the present experimental work is to explore the effects of the GNP size on the rheological properties of GNPs water and GNPs –PVA solutions at different temperatures. The shear stress , viscosity and torque are tested with different speed and shear rate at different temperature 25 ºC for GNPs-water and 38 ºC for GNPs –PVA .Using cone-on- plate viscometer type Brookfield (DV-III) Ultra. Also the shear thinning effect in nano1 and nano2, nano3 and nano4 is analyzed.

1. Materials and methods:

GNPs were synthesized by pulsed laser ablation of gold target in double distilled and deionized water DDDW and polyvinyl alcohol (PVA) solution at room temperature. The gold target (purity of 99.99%) was fixed at bottom of glass vessel containing of 1 ml of double distilled deionized water DDDW and polyvinyl alcohol (PVA). Ablation is carried out with

laser operating at 1064 nm wavelengths. The pulse energy was (550 m J, 650m J).The number of laser shots applied for the metal target at 100 pulses. The absorbance spectra of the nanoparticles solution measured by UV-VIS double beam spectrophotometer.
Fig.1 Shows the experimental setup for laser ablation of solid metal target immersed in water or PVA .The viscosity, torque, shear stress at different shear rate. Were measured using Brookfield DV-III Ultra Programmable viscometer supplied with temperature bath and controlled by a computer. Cone-on-plate viscometer setting at 25 °C and different shear rate.

The principle of operation of the Cone-on-plate viscometer is to drive a spindle (which is immersed in the test fluid) through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection. Spring deflection is measured with rotary transducer. The viscosity measured range of the DV-III Ultra (in centipoises or cp) is determined by the rotational speed of the spindle , the size and shape of the spindle , the container the spindle is rotating in , and the full scale torque of the calibrated spring .

The DV-III Ultra can also measure yield stress 0.5 ml of each GNP filled aqueous solution and PVA was poured in the sample chamber of the viscometer.

Fig.2 Shows the cone-on - plate viscometer .Torque range must be scatting in the examine (10 – 100) % correct reading.

2. Results and discussion

Fig.3 Shows the absorbance spectra of gold colloids prepared by laser ablation of a gold plate immersed in DDDW and PVA solution s at various concentrations for laser energy of (550 and 650) mJ, λ=1064 nm .The figure shows broadband in the visible region with maximum peaks around 530nm. The concentrations of GNPs for 650 mJ is higher than of 550 mJ as well as GNPs with polyvinyl alcohol (PVA) shows broadband in the visible region with maximum peaks around (525-530) nm and reaching a maximum value 0.188 in GNPs- PVA . Normally, λmax can be related to particle size it is believed that convenient amount of PVA in water will enhance the efficiency of nanoparticles formation, reduce the size and increasing the stability .
Fig.4 Shows TEM pictures and size distributions of nano1 and nano2 only, produced by laser ablation of metal plates immersed in DDDW; the laser wavelength is 1064 nm. The nano1 and nano2 shows spherical morphology and with good particle size distribution dispersed in the solution .The nanoparticles thus produced were calculated to have the average diameters of 10 nm and 20 nm at the laser energies of 550mJ and 650 mJ, respectively. The average particles sizes increase and the size distribution broadens with an increase of applied laser energy. The origin of the surface morphology of the irregularly shaped particles in case of low energy can be explained by absorption by defects and thermally induced pressure pulses which cause cracking [13].
Fig.5 Shows that the shear stress increased with the shear rate increasing and nano2 exhibits higher shear stress than nano1due to the high viscosity of nano2.The shear stress increased rapidly at 255 shear rate while change gradually after that. The 650mJ power produces higher particle size than that of 550 mJ power. The surface area and the contact distance are high for higher particle size than that for lower particle size. The viscosity increases with concentration, size and surface area increasing .The shear stress depend on the viscosity, shear rate and power index.
The rheological properties for the different GNPs sizes in aqueous solution (water) and PVA can be described by the power law model:

$$\tau = \eta \gamma^{n} .... (1)$$

Where τ is the shear stress, η is the viscosity (CP), γ is the shear rate, and n is the flow behavior index. η can be used to describe the variation in viscosity for the different GNPs sizes [14].

Fig.6 Show that the viscosity decreased with the shear rate increasing for nano1 and nano2 that called the shear thinning behavior associated with the non – Newtonian flow of Nano - fluid .The maximum viscosity magnitude occurs at low shear rate due to the accumulation and slowly nanoparticles movement .Also the viscosity drop rapidly at the first step and then decreases gradually to the final step, where the behavior become approximately stable. The viscosity magnitude of nano2 is higher than that of nano1 due to the high nanoparticle size.

Fig.7 indicates the torque increases with the shear rate increasing, due to shear stress increasing.

The figure.8 GNPS –PVA Nano-fluid shows that the viscosity of nano3 and nano4 has decreased in general with the increasing shear rate .The viscosity of Nano4 is more than Nano3. The shear thinning effect of nano4 is higher than that of nano3 shear thinning behavior is commonly associated with the non – Newtonian flow of Nano - fluid .The maximum viscosity magnitude occurs at low shear rate due to the accumulation and slowly nanoparticles movement while at high shear rate high dispersion level and alignment particles produce, which decrease the viscosity.

Fig.9 Shows that the shear stress increased with the shear rate increasing and nano4 exhibits higher shear stress than nano3 due to the high viscosity of nano4 .The shear stress increased linearly with shear rate. The viscosity increases with concentration, size and surface area increasing .The shear stress depend on the viscosity and shear rate.

Fig.10 indicates the torque increases linearly with the shear rate increasing, due to shear stress increasing.

3. Conclusions

The absorption maxima and absorption intensity are particle size-dependent. At a constant GNP size, the absorbance was found to be proportional to the concentration of gold. This is due to the increase in the number of GNPs as well as the increase in the surface Plasmon resonance of GNPs. An intense absorption peak was observed at wavelength of 525 nm which is generally attributed to the surface Plasmon excitation of the small spherical GNPs. The high energy laser ablation produces higher average Nano-gold particle size. The higher a verge GNPS diameter exhibit higher viscosity than that of lower average GNPS diameter. The GNPS – water and GNPs –PVA solutions exhibits shear thinning behavior and compatible with power law non – Newtonian viscosity .The shear thinning drop faster for nano2 and nano4 than that for nano1and nano3 due to the particle distribution style. The addition of PVA to the solution leads to the formation of smaller nanoparticles which enhances dispersity and prevents the aggregation.

5. References:

1- Dr. Nizar Jawad Hadi, Najim A and Russel Mohammed "Strengthening and Toughening of Unsaturated Polyester by Using Some Additives in Gear Application" Applied Mechanics and Material, Vol. 390, pp. 567-573, Aug. 2013.

2- D. Riabinina, J. Zhang, M.d Chaker, J. Margot and D. Ma, (2012). Size Control of Gold Nanoparticles Synthesized by Laser Ablation in Liquid Media,ISRN Nanotechnology, Article ID 297863, 5 pages.

3- M. Chinna , P. R. Devi, A. Sara vanakumar ,V. Femi , E. Hemananthan , S. S. Rani (2012). Synthesis and characterization, of gold nanoparticles by justicia gendarussa burm f. leaf extract Chinna et al., IJPSR, and Vol. 3(2): 623-629.

4- F. Hajiesmaeilbaigia, M. Fazeli Jadidi,A. Motamedi (2012). Synthesis and Characterization of Au–Zn Nanoalloy by Laser Irradiation in Liquid Media, Vol. 121 acta physica polonica , No. 1.

5- M.Kalyva,G.Bertoni,A.Milionis, R.Cingolani and A. Athanassiou, (2010). Tuning of the Characteristics of Au Nanoparticles Produced by Solid Target Laser Ablation into Water by Changing the Irradiation Parameters, microscopy research and technique 73:937-943.

6- Besner S, Kabashin AV, Winnik F M and Meunier M.. (2008)."Ultrafast laser based ‘‘green’’ synthesis of non-toxic nanoparticles in aqueous solutions", Appl Phys A 93:955–959 Natalie.

7- P. Praetorius and Tarun K. Mandal, (2007). Engineered Nanoparticles in Cancer Therapy, Recent Patents on Drug Delivery & Formulation, Vol.1 and No. 1.

8- Shima. P. D (2011). Synthesis, Characterization, Thermal and Rheological Studies in Nanofluids , Tamil Nadu, India, Kalpakkam-603 102.

9- Asis Patanaika, Rajesh D. Anandjiwalaa, R.S. Rengasamyc, AnindyaGhoshd, and Harinder Pale, (2007). Nanotechnology in fibrous materials – a new perspective , Vol. 39, No. 2, 67–120.

10- C.L. Casper, J.S. Stephens, N.G. Tassi, D.B. Chase, and J.F. Rabolt, (2004). Controlling surface morphology of electro spun polystyrene fibers: Effect of humidity and molecular weight in the electro-spinning process, Macromolecules , 37 pp. 573–578.

11- Manfred L., Hallensleben "Polyvinyl Compounds, Others" in Ullmann's Encyclopedia of Industrial Chemistry, 2000, Wiley-VCH, Weinheim. doi:10.1002/14356007.a21_743

12- Fromageau, J.; Brusseau, E.; Vray, D.; Gimenez, G.; Delachartre, P.(2003) Characterization of PVA cryogel for intravascular ultrasound elasticity imaging; IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control, Volume: 50, Issue: 10. Page(s): 1318 - 1324.

13 - O.R. Musaev, A.E. Midgley, J.M. Wrobel, M.B. Kruger, (2010). Laser ablation of alumina in water, Chemical Physics Letters 487, 81–83.

14 - Mohamed Anwar K Abdelhalim, Mohsen M Mady, and Magdy M Ghannam, (2011).Rheological and dielectric properties of different gold nanoparticle sizes, PMC Journals, Lipids Health Di, 10: 208.

15- Prof. Dr. Ihsan Y. Hussian and Nizar Jawad Hadi "An investigation into three dimensional turbulent flow of Newtonian liquid in stirred tanks mixers" No. 1, Vol. 16, 2010.

16- Dr. Nizar Jawad Hadi, Najim A. Saad and Dhay Jawad Mohamed "Study The Effect of $CaCO_3$ Nanoparticles on The Mechanical Properties of Virgin and Waste Polypropylene" Advance Material Research, Vol. 1016, PP 23-33, 2014.

17- Dr. Nizar Jawad Hadi ,Dr. Jaleel Kareem Ahmed and Ula Ali "The effect of polymer on the morphology and rheological behavior of silver nanoaqueous solution" journal of applied science, 2016.

18- Dr. Nizar Jawad Hadi, Najim A. Saad, Zainab A.A Saadi"Study the Rheological Behaviour of PP- Runner Waste Blends towards using for Medical Syringes Production" International Journal of Engineering and Technology Volume 3 No. 10, October, 2013.

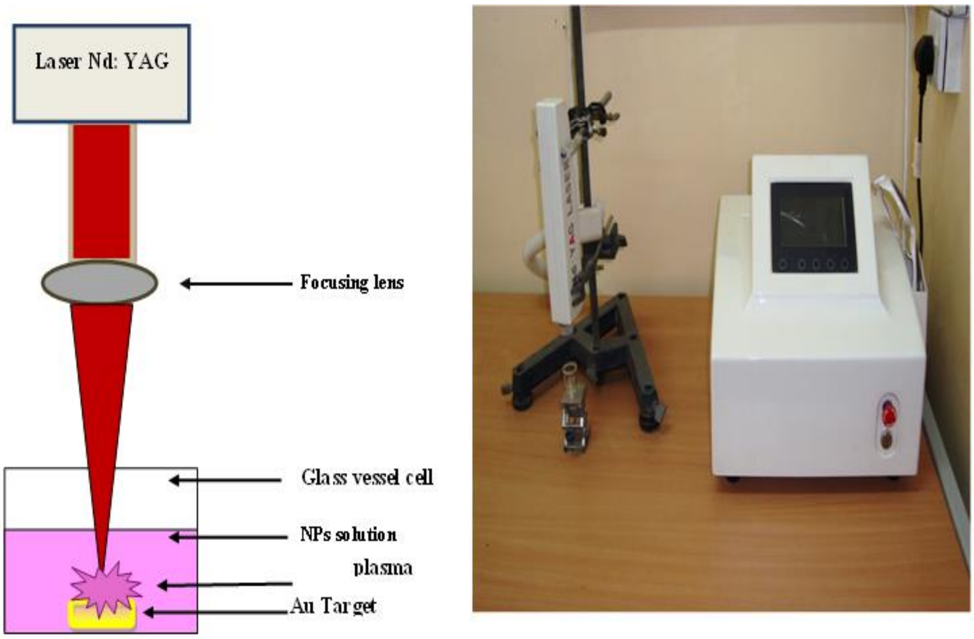


Fig. 1: Experimental setup for nanoparticles synthesis by PLAL process.

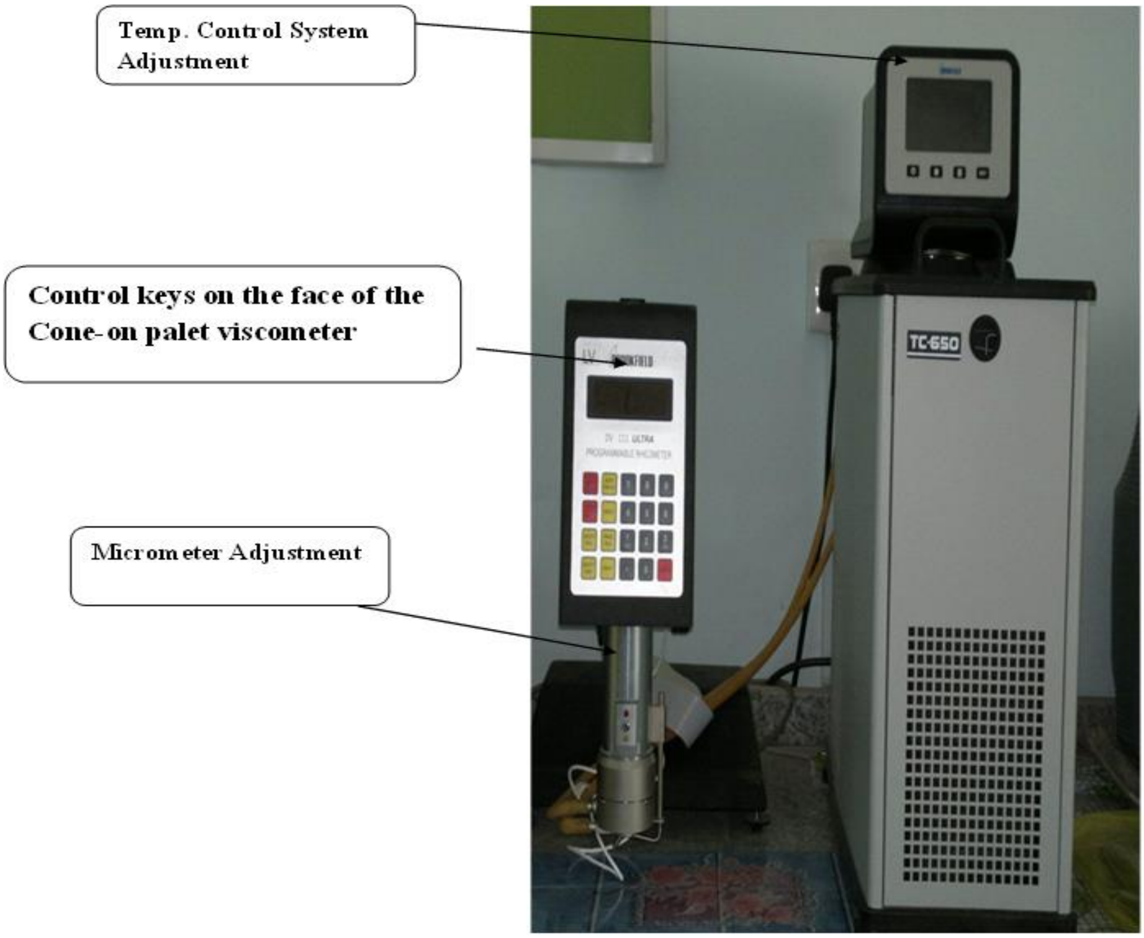


Fig.2 Cone-on – plate viscometer

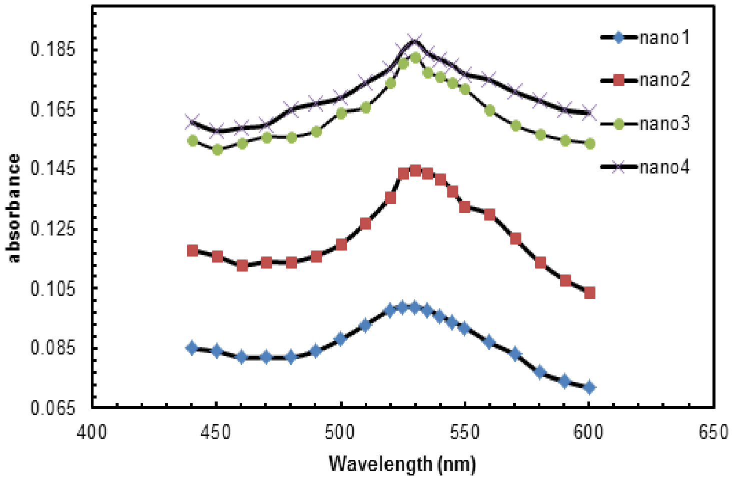


Fig.(3) Absorbance spectra of Gold nanoparticles obtained by laser ablation of metal plate immersed in DDDW and PVA with laser energy of (550 to 650) mJ/pulse

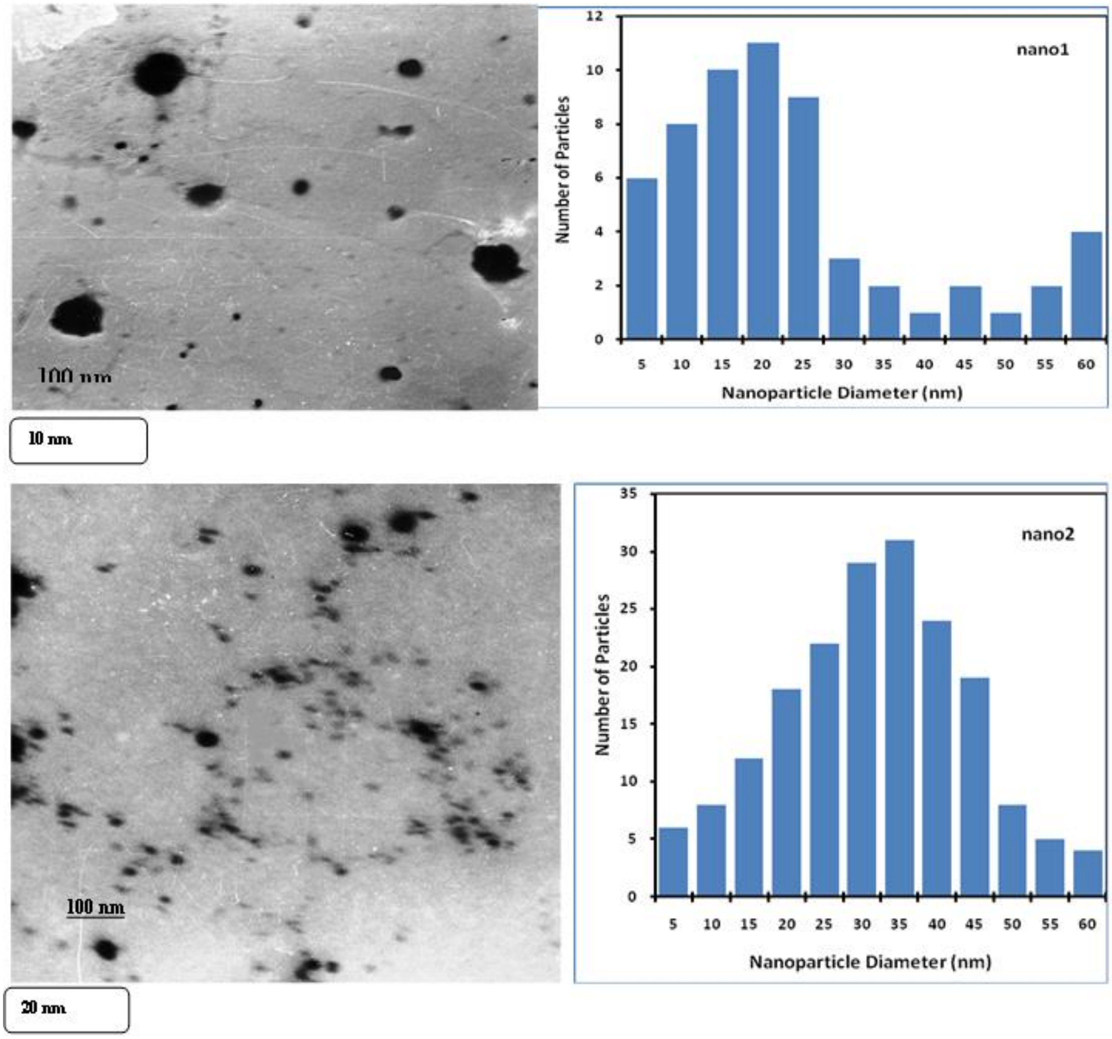
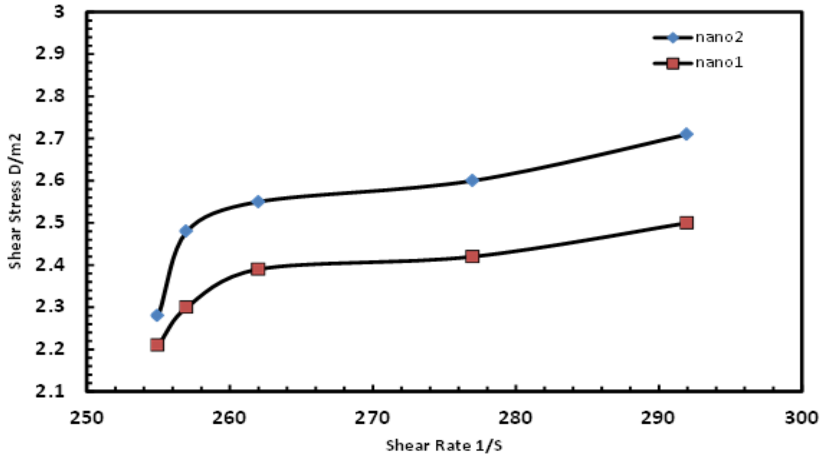


Fig.4: TEM images and size distributions of nano1 anno2



Fig, (5) . The relation between shear rate 1/s and shear stress D/m2 for nano1 and nano2 at 25°C.

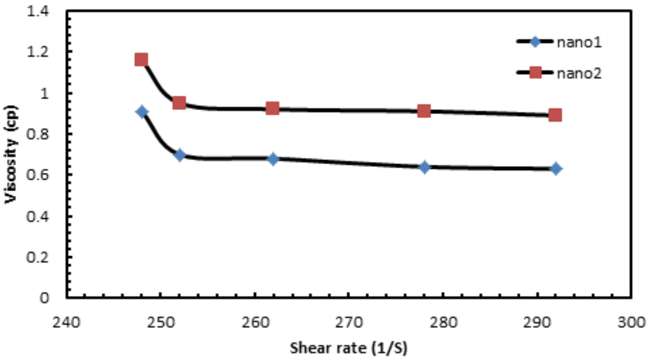


Fig. (6) .The relation between Viscosity and Shear rate for nano1 and nano2 at 25°C

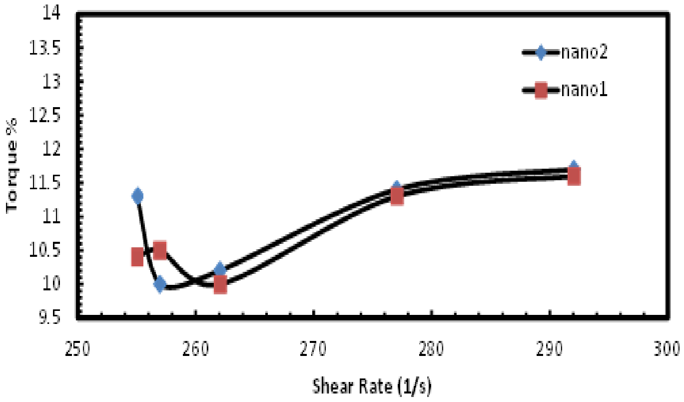


Fig.(7). The relation between Torque and shear rate for nano1 nano2 at 25°c.

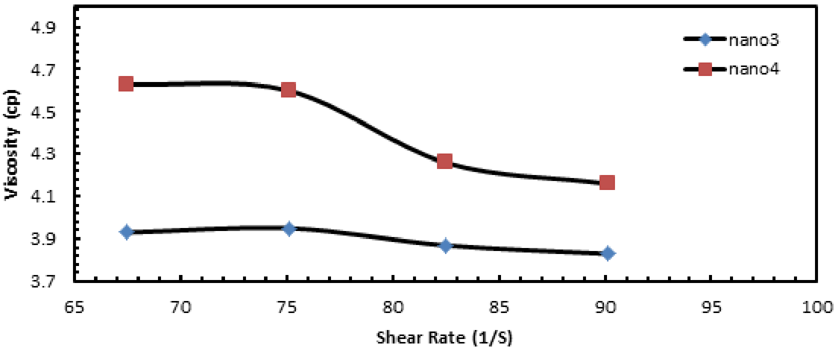


Fig. (8) .The relation between Viscosity (CP) and Shear rate (1/S) for nano3and nano4 at 38°C of GNPs in PVA.

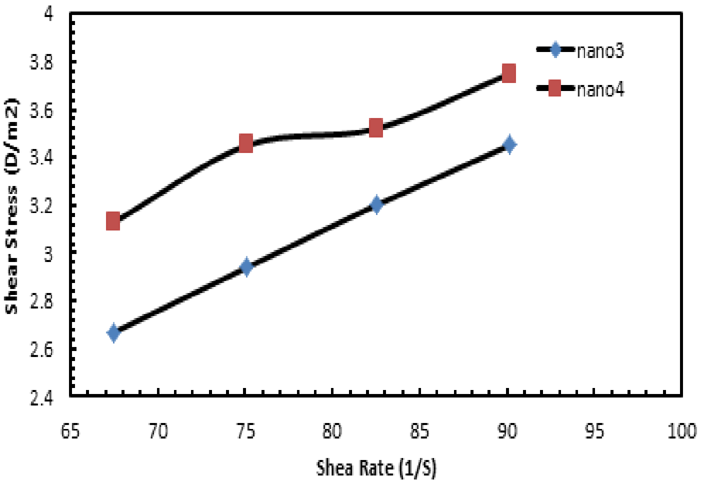


Fig.(9).The relation between shear rate (1/s) and shear stress (D/m^2) for nano3 and nano4 at 38°C.

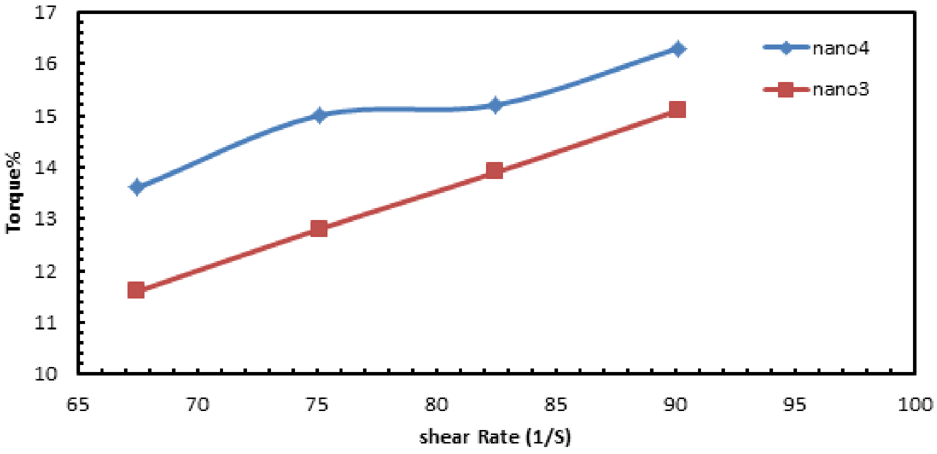


Fig.(10). The relation between Torque and shear rate (1/s) for nano3 and nano4 at 38°c.