The effect of polymer on the morphology and rheological behavior of silver nanoaqueous solution

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ABSTRACT

This work studies the effect of biopolymer on the flow behavior and morphology of silver nanoparticle (SNP) dispersed in aqueous solutions using laser ablation technique. Polymer structures have the ability to control on the nanoparticles formation and flow properties of polymer nanosolution. Different concentration of Powder and granules polyvinyl alcohol (PVA) and corn starch are used to prepare the base solutions. Silver target with 99.99% purity is immersed in biopolymer solution. Nd:YAG laser ablation used to prepare polymer nanofluid at 20 pulses, 8ns pulse duration, 532nm wavelength and 600 mJ energy for each polymer. Absorbance spectra of (SNP) solutions were measured by UV-VIS spectrophotometer. The morphological properties of nanosolutions are tested using atomic force microscopy AFM. The rheological behavior was investigated using cone-on-plate viscometer and surface tension device. The results show that the absorption peak of Plasmon at 400 nm indicated that the (SNP) are present. This peak shifted to the left as the (PVA) and starch concentration increases. This means that the (SNP) efficiency formation increases and (NP) size and broadness decrease. The AFM results show that the size of nanoparticles decreases as the biopolymer concentration increasing. The viscosity and surface tension increase with the biopolymers concentration and (SNP) size decreasing respectively. The absorption intensity decreases and viscosity increases after one month due to the agglomeration of (SNP). The absorption spectrum show a small change in the fresh sample compared to aged sample in 1.2g of PVA powder, and 0.25, 0.5g of PVA granules. It shows that the Ag-NPs in 1.2g PVA powder solution and 0.25, 0.5g PVA granules more stable than that of other polymer used. There is a good compatibility between optical, rheological and morphological tests.

Keywords: SNP, biopolymer, laser ablation, nanofluid.

1. Introduction

Nanofluids are liquids with stable suspension of nanometer sized particles (1–100 nm). The nanoparticles used in nanofluids are naturally made of metals, carbides, oxides, or carbon nanotubes. Water, polymer solution and oil are different types of base liquids for nanofluids. Studies from the past decade appearance that this new class of composite fluid exhibition much higher thermo physical properties such as thermal conductivity and diffusivity as compared to the base fluid (Sridhara V, Satapathy LN, 2011).

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. The amount of mass liberated was depending on the laser parameters such as: wavelength, energy, pulses, pulse duration, target properties and the surrounding environment (C. Liu, 2005, Q. Xia and S. Y. Chou, 2010).

Mostly silver has attracted much than others metals due to its unique properties which can be incorporated into antimicrobial applications, and to their surface Plasmon resonance related properties that are strongly useful for their biological applications (Hassan Korbekandi and Siavashhravani, 2012). Silver is a safe inorganic, nontoxic, antibacterial agent used for centuries and is capable of killing about 650 types of diseases caused by microbes (Brigger,I.,C.Dubernet and P.Couvreur, 2002). Polyvinyl alcohol (PVA) is a water soluble synthetic polymer. It has the formula [CH2CH (OH)] n and commonly used in medical devices due to its low protein adsorption characteristics, biocompatibility, good water solubility, and chemical resistance. Starch has been widely used due to its low cost and biodegradable polymer and occurs widely in plants (Nur Fatin Nadiah Binti Jamil, 2013).
Starch is a polymer of six carbon monosaccharide- D-glucose as a single helix structure (L. Janssen, L. Moscicki, 2009). Biopolymer used instead of distilled water because in the biopolymer case, the formation efficiency of (NPs) is improved and particle sizes are decreased as well. On the other hand, in comparison with the distilled water, the synthesized Ag NPs in aqueous solution of (PVA) biopolymer are more stable over a long period (Halimah Mohamed. et al., 2014).

In 2008 Suraj Kumar Tripathy PVA capped silver NPs were produced by a chemical reduction method. In 2011 Kanikireddy Vimala et al fabrication of chitosan-poly (vinyl alcohol)-silver nanocomposite films due to their increasing applications as antimicrobial packaging, wound dressing and antibacterial materials. In 2011 Reza Zamiri et al Silver nanoparticles inside the starch solution have been well prepared by laser ablation of a silver plate immersed in starch solution.


The aim of this work is to prepare nanofluids of different NPs- biopolymer solutions using laser ablation technique. Also to reduce the broadness and increase the efficiency of the (SNPs) formation using the polymer chains effects. Viscosity, surface tension and density were examined to support the tested structure of nanofluids.

2. Materials and methods

Different biopolymer granules and powder PVA and starch are used in this work. Silver target 99.99 % purity with dimensions of 20*5mm is provided from China Company. The nanofluids are prepared by dissolved of 1g of PVA powder in 50ml of double distilled and deionized water (DDDW) at 80°C for 30 min. with agitation using magnetic stirrer. The silver target was fixed at the bottom of the vessel containing biopolymer solution. Ablation is carried out with laser operating at 532nm and 600 mJ pulse energy. The number of laser shots applied for the metal target 20 pulse and pulse duration 8ns .SNPs/DDDW solution (S), SNPs/PVA powder solution (S1), SNPs/PVA granules solution (S2) and SNPs/starch solution (S3). Repeat steps of preparation for (2and 3g) of PVA and (0.25, 0.5and 1g) of starch and granules PVA.

Characterization

UV – VIS double beam spectrophotometer: SHIMADZU spectrophotometer UV-1800 is used to check the absorbance of the nanopolymer solutions. Also any change in concentration, size, shape and agglomeration can be predicted in this device.

Atomic force microscopy (AFM)
The morphological studies of the (SNP/PVA) and starch solutions were conducted by tapping mode AFM (AA3000) in Ministry of Science and Technology. The Nano solutions were spread on preheated mica and expose to air to dry. 2D, 3D of SNPS hages and average size distribution are obtained. Range of broadness, dispersion stability and agglomeration size can be examined also.

Cone – on- plate viscometer:
The rheological measurements are performed with cone on plate viscometer. The cone diameter 25mm and its angle of 0.8 .All experiments are conducted at a constant gap of 0.5mm and an initial stabilization period of 2 minutes is given for achieving temperature equilibration. Viscosity of SNPS solution at different concentration of PVA and starch was tested.
Surface tension
Surface tension measurements obtained using JZYW-200B Automatic Interface Tensiometer supply by BEING UNITED TEST CO., LTD. The surface tension of SNPS solution was examined at different concentration of PVA and starch.

Field Emission Scanning Electron Microscopy (FESEM):-
The surface morphology and distribution of nanoparticles through film of SNPS-PVA performed on small pieces taken from the impact samples using a low voltage FESEM (model MIRA 3 XM4, USA) in Al-Razi Institute in Iran. The fracture surfaces of impact samples are coated with a thin layer of gold before test the photographs are taken at different magnification.

3. Results and discussion

UV – VIS spectrophotometer
Fig. 1 shows the uv-vis spectrophotometer of silver nanofluid with different concentration of (PVA) powder prepared by Nd-YAG laser ablation method. Positions of the SPR bands change according to the PVA powder concentration from 1g to 3g. When the concentration increases from 1g to 3g, the position of SPR changed from 401nm to 402 nm. The arrangement of concentration according to intensity from bottom to top is 1g -2g and 3g, due to the molecular weight value, viscosity and density increasing. At region over 600nm the lower curve means lower agglomeration. This is due to the increasing of viscosity and density. The absorbance peak of 1g, 2g and 3g at about 400nm indicates that the SNPS is generated in the solution with spherical shape (Halimah Mohamed et al, 2014, Alireza HOJABR et al, 2014). Also the color of solution changes from light to yellow due to the generated of SNPS in the solution (Pichitchai Pimpang et al, 2008). The absorbance intensity increases with the increasing of PVA concentration.

The Figs. 2and 3 show the uv-vis spectrophotometer of SNPS with different concentration of PVA granules and starch respectively prepared by Nd-YAG laser ablation at energy 600MJ and 20 pulse. The SPR bands changed from 402 to 396 nm due to increasing of PVA granules from 0.25g to 1g. The efficiency of SPR increased due to the blue shifting. These results are compatible with the Mie theory (REZA ZAMIRI et al, 2012, Bohren C F and Huffman D R, 1940, Ibrahim M El-Sherbiny, et al, 2013). The viscosity and density increasing prevent the SNPS to grow up and agglomerate. For starch in Fig. 3, SPR bands increased from 396 to 400nm because the concentration of starch increased from 0.25 to 1g. The slight increasing of viscosity and density with the starch increasing is not sufficient to control on the SNPS size. However the SNPS in this solution is still around 400nm and less. This means the best starch concentration is 0.25g, due to the blue shift at 396nm.

4. Morphology
Fig. 4, A and B Show the 2D and 3D AFM images of SNPs particle size in water. Fig 4, C shows the average size distribution of SNPs. However the nanoparticles have shape approximately between irregular and spherical. The broadness of nanoparticles is starting from 30nm and rises up to the 200 nm. In general agglomeration also observed in this images.

Fig. 5, A and B Show the 2D and 3D AFM images of particle size of SNPs at 1g S1 solution. The maximum size and high of nanoparticle are about 9nm and 4.1nm respectively. Fig. 5, C indicates the average size distribution of SNPs. Broad distribution produced with the range from zero up to 180nm. The average particle size of 1g PVA S1 is 83nm, which is bigger than that of 65nm for the 3g PVA S1 due to the increasing of biopolymer concentration. The significant increasing of viscosity and density controls on SNPS broadness and size. However the nanoparticles have approximately spherical or Circular shape. The particle size indicates lower agglomeration and more homogenous than that of Fig.4. The broadness starts from zero up to 180 nm and the most particle size concentrated between 20 and 70nm, which is lower particle size and lower broadness range than that for SNPS - water solution.

Fig. 6, A and B indicate that the SNP less agglomeration and higher homogeneous distribution. Fig 6, c shows the broadness range starting from zero up to 100 nm. The average size range indicates SNPs over 100nm is negligible, due to the viscosity and density increasing of 3g PVA solution. The particle size decreases and the most SNPS concentrated between 30-40nm this result compatible with the uv-vis results in Fig. 1, where the absorbance intensity increasing and peak wavelength decreasing from 402 to 396nm, due to the particle size reduction.

Fig.7 A, B Shows 2D and 3D AFM images of particle size of SNPS at 0.25g PVA granules solution. Fig. 7, C indicates the average size distribution of SNPS. Broad distribution produced with the range from zero up to 350nm. The significant increasing of viscosity and density controls on SNPS broadness and size. However, the nanoparticles have approximately spherical or irregular shapes. Fig.8 A, B Shows 2D and 3D AFM images of particle size of SNPs at 1g
PVA granules solution. Fig.8.C indicates the average size distribution of SNPs. Broad distribution produced with the range from zero up to 240nm. It was shown that with increasing the concentration of biopolymer from 0.25g to 1g the broadness decreases from 350nm to 220 nm and the size of nanoparticle also decreases due to increasing of biopolymer concentration and reduction of the particle diameter. The particle size over 100nm in Fig. 8 is higher than that of Fig. 7, due to the agglomeration illustrated in the topography images and uv-vis of Fig.2.

Fig.9, A SHOWS the topography images of the surface and particles size of SNPs in 0.25g S3 solution in 2-D. Nanoparticles with different shapes but most of its have spherical shape is present. The average size of 0.25g S3 is 95nm which is bigger than that in the 1g of S3 as illustrate in Fig.10.A, due to the increasing of biopolymer which is controlled on the particle size grows up this agree with the result of (Majid Darroudi, 2011) Fig.9. B, Fig.10. B: 3D particle size distribution images of SNPs with 0.25g and 1g of S3 show the agglomeration clearly. Particles size distribution extracted from the images can produce accurate information as shown in Fig.9C, Fig. 10 C. A small reduction in broadness range observed due to the starch quantity increasing. The particle size is not well shown because of the nature of starch solution and low viscosity value these results confirmed with that in Fig. 3.

**Viscosity**

Fig.11 indicates that the viscosity increasing with PVA powder increasing due to the high molecular weight of this polymer solution. The increasing of PVA powder from 1g to 3g increases the viscosity from 10 to 35cp. These results confirmed with the behavior of this solution in uv-vis and the structure in Figs. 1, 5 and 6. The peak position decreases from 400 to 396 due to the viscosity increasing. Fig.12 shows that the viscosity increases from 2 to 7.5cp due to the PVA granules increasing from 0.25 to 1g. Fig.13 illustrates that the viscosity decreases at 0.25g starch, then increasing with the starch increasing to return to the origin value. This result is compatible with that in 3, 9 and 10 for uv-vis and AFM respectively.

**Density**

Fig.14 shows that the density decreases at 1g and 2g then increasing at 3g PVA powder solution. This result compatible in general with viscosity at Fig. 11. Fig. 15 indicates a slight decreasing of density at 0.25 and 0.5g then increases at 1g PVA granules. A gain this result compatible in general with the viscosity behavior at Fig.12. Fig. 16 indicates decreasing of density at 0.25g of starch percentage. After 0.5% starchy the density keep stable approximately. The density decreases along with the starch increasing. This behavior is compatible with the viscosity decreasing at Fig. 13.

**Surface tension**

Figs. 17 and 18 show that the surface tension increases with PVA powder and granules increasing. The increasing in surface tension occurs due to the SNPS size reduction. The lower SNPS size produces higher surface free energy. This result in Fig. 17 confirmed with that at Figs. 1, 5, 6 and 11 for powder PVA and the results at Fig.18 confirmed with that at Figs. 2, 7, 8 and 12 for granules PVA where the absorption intensity increased, SNPS decreased, and the viscosity increased respectively.

Figs. 19 indicates that the surface tension decreases at 0.25g of starch and then keep stable up to the 1g . The surface tension decreases because the polymer chains covers the particles and separated from the surrounding fluid which increases the electrostatic force between the particles as in (Saad Tanvir and Li Qiao, 2012) work. The increasing in surface tension occurs due to the Van der Waals force between SNPS. Both viscosity and surface tension tests are used as indicators for stability of nanofluid and the homogeneous degree of nanoparticles distribution

**Stability of nanofluids**

The uv-visible spectra of the SNPs in PVA powder and granules solutions were measured after 1month to investigate the stability of nanofluids (M. Tajidizadeh et al, 2014). Fig.20 and 21 show that the absorption intensity decreases and viscosity increases after one month due to the agglomeration of SNPs. The decreasing in absorption intensity is inversely proportional to the viscosity increasing and agglomeration. Therefore the 2g and 1g PVA powder solution are more stable than that of 3g PVA powder solution and 0.25g, 0.5g PVA granules solutions are more stable than that of 1g . The absorption spectrum in Fig.20 shows a small drop in the fresh sample compared to the aged sample in PVA powder solution at 1 and 2g, while a large drop occurs at 3g. Fig.21 indicates that at 0.25 and 0.5g also a small drop in absorbance intensity occurs, while a large drop takes place at 1g. Moreover, there is a red shift which indicates some agglomeration of the SNPs at 1g granules PVA due to the slight sedimentation of the larger particles. Also viscosity for each type increases after 1 month aging. There is a good confirmation between a and b tests, where amount of dropping in absorbance intensity proportional with a mount of viscosity increasing.
Filed Scanning electron microscopy was utilized to study the morphological property of polymeric films doping with SNPs of 20 and 100 pulses of laser ablation. Fig.22.A shows the morphology and surface nature of SNPs-PVA powder film prepared by evaporating technique of 20 pulses. Fig.22B shows FESEM images of SNPs- PVA powder films with 100 pulses, the nanoparticles displayed nearly spherical shapes and did not show any aggregations. The spherical nanoparticles could be observed, for both 20 and 100 pulses. The particles were closed and sorted out well from each other without adhesion or cohesion. The surface was relatively smooth.

Fig.22 A shows the morphology and surface nature of SNPs-PVA granules film prepared by evaporating technique with 20 pulses. Fig.22B shows FESEM images of filled SNPs- PVA granules films with 100 pulses. The nanoparticles from all have spherical shapes.

5.Conclusions
The results show that the absorbance peak around 400nm generates the SNPS.uv-vis also shows that the absorbance intensity increases with the PVA powder, granules and starch solutions increasing. The generation of SNPS in water or polymer solution using laser ablation is easy, simple, save, low cost, stable and one step nanofluid preparation method. The broadness of the nanoparticle in the solution is a major problem in this method. Adding of PVA and starch polymers to the water improve the formation efficiency and reduce the broadness of SNPS .AFM results show that with the increasing of biopolymer concentration the average size of SNPS decreases because the biopolymer control on growth up of the particles size. Also with concentration of biopolymer increasing, the viscosity increases due to the viscous nature of polymer. The density behavior compatible with the viscosity increasing .Both viscosity and density improving the efficiency of SNPS formation.3g PVA powder and 1g starch solutions indicate the best broadness, due to the higher viscosity and density. The viscosity and surface tension give an indication whether the nanosolution is stable and high dispersion of SNPS occurs or not. The surface tension increases with the decreasing of SNPS and broadness. The absorption intensity decreases and viscosity increases after one month due to the agglomeration of SNPS. The decreasing in absorption intensity is inversely proportional to the viscosity increasing and agglomeration. It shows that the Ag-NPs in PVA powder more stable were the absorption spectrum does not show a significant change in the fresh sample compared to aged sample, but a large reduction in 1g PVA granules was found. Strong relation between morphology and rheological behavior of SNPs-PVA and starch solution is obtained.
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Fig3: UV-VIS spectrophotometer of $S_3$ of 0.25, 0.5 and 1 g of starch solution

Fig. 4: Topography of S (A) 2-D particle size (B) 3-D particle size (C) particle size distribution
Fig. (5): Topography of the Si-1gPVA (A) 2-D particles size (B) 3-D particle size (C) Particle size distribution.

Fig. (6): Topography of the Si-3gPVA (A) 2-D particles size (B) 3-D particle size (C) Particle size distribution.
Fig. 7: Topography of SNP$_x$ - 0.25g PVA granules (A) 2-D particle size (B) 3-D particle size (C) particle size distribution.

Fig. 8: Topography of SNP$_x$ - 1g PVA granules (A) 2-D particle size (B) 3-D particle size (C) particle size distribution.
Fig.(9): Topography of Si-0.25g starch (A) 2-D particles size (B) 3-D particles size(C) particle size distribution.

Fig.(10): Topography of Si-1g starch (A) 2-D particles size (B) 3-D particles size(C) particle size distribution.
Fig 11: Viscosity behavior of $S_1$ solution with the PVA powder increasing

Fig 12: Viscosity behavior of $S_2$ solution with the PVA granules increasing

Fig 13: Viscosity behavior of $S_3$ solution with the starch increasing
Fig 14: Density behavior of \( S_1 \) with the PVA powder increasing

Fig 15: Density behavior of \( S_2 \) with the PVA granules increasing

Fig 16: Density behavior of \( S_3 \) solution with the starch increasing
Fig 17: Surface tension behavior of $S_1$ with the PVA powder increasing

Fig 18: Surface tension behavior of $S_2$ with the PVA granules increasing

Fig 19: Surface tension behavior of $S_3$ with the starch increasing
Fig. 20(a) UV-visible absorption spectra and (b) viscosity of SNPs in 1, 2 and 3g of PVA powder solutions for freshly prepared and after 1 month aging.
Fig. 21(a) UV-visible absorption spectra and (b) viscosity of SNPs in 0.25, 0.5 and 1 g of PVA granules solutions for freshly prepared and after 1 month aging.
Fig. 22: (A-B) scanning electron images of SNP₃ - PVA powder solution thin films.

Fig. 23: (A-B) scanning electron images of SNP₃ - PVA granules solution thin films.