ORIGINAL ARTICLE

Flow Behavior of Poly (vinyl alcohol)/Aluminum Oxide Nanoparticles Solutions as Novel Method to Control the Viscosity

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ABSTRACT

In this research, the flow behavior and stability of Aluminum oxide (Al_2O_3) nanoparticles(NPs)/Poly (vinyl alcohol) (PVA) solutions were studied. PVA was mixed with 0.5, 1, 1.5 and 2 weight percent (wt. %) of AL_2O_3 NPs. The cone plate rheometer was used to check the viscosity, due to the shear rate and concentration. The results show that the viscosity of PVA/AL_2O_3 NPs solution increase with the increase of shear rate, shear thickening, while decrease with the concentration. Then, the results fit to the fluid models by using a Rheocalc program. The flow behavior of the Poly(vinyl alcohol)/AL_2O_3 NPs solutions displayed solution characteristics that closely agreed with the Herschel–Bulkley fluid model. Beside that, the samples were examined also by other tests, such as Tensometer and pH meter, to predict and explain the flow performance mechanisms. In addition, after solvent evaporation, the solid samples were tested by the atomic force microscope (AFM) to understand the stability of Al_2O_3 NPs in the solid state and prove prediction technique more deeply, while the force attractions between polymer chains and NPs were figured out by Fourier-transform infrared spectroscopy (FTIR).
Keywords: Flow Behavior, Poly vinyl alcohol, Viscosity, Al_2O_3 Nanoparticles, shear thickening flow,

INTRODUCTION

Viscosity, shear rate and shear stress of biopolymer solutions are an important parameter in biomedical applications, for example in controlling on entrap to and release of the drug during drug delivery technique[1]. Besides that, it is well established above a certain threshold value for the molar mass Mc, the terminal (zero shear) viscosity of polymer melts scales with molar mass to the power 3.4. The strong increase of the viscosity with increasing molar mass is related to entanglement coupling and the presence of a physical entanglement network characterized by an average molar mass between the physical cross-links, Me, between the macromolecules. This viscosity–molar mass dependence implies that polymers of low molar masses are preferred for processing; however, high molar masses are required for materials properties, notably toughness and strength. One way to improve the properties of polymeric materials other than increasing molar mass is to use additives such as nanofillers[2].

According to Einstein[3],the addition of particles to a liquid lead to an increase in viscosity. This has also been experimentally confirmed for polymer melts and solutions. The increase in viscosity may limit the process ability. However, anumber of researchers recently found that the melt viscosity of polymers can be reduced by using nanoparticles[4]. Several processing techniques to disperse nanoparticles into a polymer matrix have been explored, including in-situ preparation, solution processing and melt compounding[5-12].The in-sit preparation can be divided into two routes: in-situ polymerization in the presence of nanoparticles and in-situ synthesis of the nanoparticles in the polymer matrix[9-14]. Dispersion of nanoparticles via solution processing is another technique that is frequently used.

Vollenberg et al. were able to produce sufficiently well-dispersed poly (imide)-organophilic clay nano composites by dissolving poly (imide) and the clay particles in a polar solvent for several hours. Then, the mixture was solvent casted to allow the solvent to evaporate[5].Tuteja et al. demonstrated that rapid precipitation after solution mixing facilitated a better dispersion of functionalized magnetic nanoparticles compared to the more conventional solvent evaporation. Excellent silica dispersions were achieved by Bansal et al. via a toluene solution mixing of poly (styrene) (PS) with untreated or low molar mass PS-grafted silica nanoparticles. They showed that the choice of the solvent strongly affected the nanoparticle dispersion.[15] Roberts et al. observed a decrease in viscosity by blending small silicate clusters with a radius of approximately 0.35 nm in poly(dimethylsiloxane). Since the particle size approaches the length scale of the monomer, the decrease of the viscosity may be attributed to plasticization[15]. Later, Xie et al[16] discovered that at high shear rates (>100 s-1), the viscosity of poly(vinyl chloride) (PVC)/calcium carbonate (CaCO3) nano composites was lower than that of pure PVC and the viscosity continued to decrease with increasing CaCO3 nanoparticle concentration. The authors explained the decrease in viscosity by a "ball-bearing" effect of sphericalnanoparticles. When spherical particle-filled polymers are introduced to a shear flow, a high local shear is developed in the narrow gaps between two nearby rotating spherical particles, which may cause the chains to disentangle. At sufficiently high shear rates, the viscosity decreases as the induced local shear in the gaps increases and chains become more

disentangled. A shift in the Tg of the PVC/CaCO3 Nano composites towards higher temperatures and an improvement in mechanical properties were also observed by Xie et al[16]. Similarly, Chen et al[17]. and Lai et al[18]..observed a decrease in viscosity when they added micron-sized particles (glass-beads and barium sulfate) to pure poly(carbonate) (PC). This decrease was also interpreted by the authors with the help of the 'ball-bearing' effect[18].S. Geng, was reported a method based on in situ polymerization to synthesize nanocomposites of well-dispersed cellulose nanocrystals (CNCs) and poly(vinyl acetate) (PVAc)[19].Mackay et al[20] reported a decrease in viscosity by blending linear PS with organic particles, synthesized by intra molecular cross-linking of PS chains. The authors attributed the decrease in viscosity to the excluded free volume introduced by the nanoparticles. This decrease in viscosity was accompanied by a significant decrease in the Tg, which may also have an impact on the final properties. The viscosity decrease was only observed for entangled.[15] Wang et al[21]also explained the decrease in viscosity of PC/CaCO3 Nano composites based on the excluded free volume induced by the CaCO3 nanoparticles, which was confirmed by a Tg depression. Y. Tan, has been studied the rheology of small amount (0.5 wt. %) of reduced graphene oxide to poly(vinyl alcohol) in the dilute regime of filler, resulted in a fourfold decrease in steady viscosity at 0.01 s[22].

W. Tian, has been discovered the improved nanoflow behaviours of polystyrene melts in ordered porous alumina templates with the addition of silica nanoparticles[23].Jain et al. found that by using less than 1 wt. % silica nanoparticles produced via insitu sol-gel reactions, the melt viscosity of iPP decreased by as much as one decade, while no decrease in Tg was observed. The viscosity decreased with increasing silica content up to 0.5 wt. %; subsequently, the viscosity increased on further increasing the silica content. Moreover, the decrease in viscosity was achieved without sacrificing the mechanical properties. Jain et al. attributed this effect to selective adsorption of the high molar mass chains on the nanoparticle surface, where the nanoparticles were surrounded by high molar mass chains, and the matrix consisted of low molar mass chains[24]. In summary, four different mechanisms have been reported in literature to explain the decrease in viscosity when nanoparticles are added to the polymer matrix: the 'plasticizing' effect[19],the 'excluded free volume[15,21,22]',the 'ball-bearing' effect,[18-20]and the 'selective adsorption' mechanism[2] to date, there are continuing disputes on the exact mechanism to explain the decrease in viscosity and it remains a challenge for theoreticians.

This work aims to study the effect of inorganic (Al_2O_3) nanoparticles (NPs) on biopolymer solutions (Polyvinyl alcohol (PVA)), viscosity, stability and flow behaviour. PVA will mix with 0.5, 1, 1.5, and 2 Wt. % of Al_2O_3 NPs. The cone plate viscometer will use to test and study the viscosity behaviour aswell as determine the best fit of a mathematical model. The samples will examine also by other tests to explain the decrease in viscosity and flow behaviour more deeply, as well as to identify the mechanisms for that. Firstly, density test to explain the effect the 'excluded free volume' mechanism, while Tensometer used to give indicator if themechanism of plasticizingeffect will have role. Also, atomic force microscope will use to show the 'ball-bearing' effect as the mechanism of solid state. Finally, pH meter and FTIR spectroscope were check the samples to understand the 'selective adsorption' mechanism.

MATERIALS AND METHODS

Materials: All materials were used as obtained without any further purification or modification. Polyvinyl alcohol (PVA) having a Viscosity (22-30) mPa.s and pH equals to 5-7 , was supplied in powder form by Changzhou haijian new textile materials CO.LTD/china. Nano Alumina Oxide (Al2O3) was supplied in Nano powder form by Shanghai Yuefang Industry & Trade Development Co., Ltd. Shanghai, China.

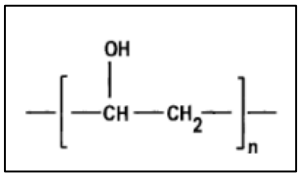


Fig. 1:Schematic structure of PVA.

Samples Preparation Polyvinyl alcohol Solution Preparation of PVA & H_2O at 5 weight percentage wt. % of PVA powder. Solutions Preparation of PVA were using an accurate weight equipment and mixed with magnetic stirrer at temperature 70 C° for 30 minutes. Then, samples of PVA/Al_2O_3 NPs, figure 2, were prepared through addition of Al_2O_3 NPs at (0, 0.5, 1, 1.5 and 2) wt.% by using glove box for safety as shown in figure 3. After that, it is mixed by magnetic stirrer at temperature 50 C° for 45 minutes.

Equipment

Cone-Plate Rheometer: The flow behaviour was studied by using "BROOKFIELD" cone on plate viscometer measurement, show in figure 4. The simple cone and plate rheometer geometry, figure 5, provides a uniform rate of shear and direct measurements of the first normal stress difference. It is the most popular instrument for measurement of non-Newtonian fluid properties. The working shear stress and shear strain rate equations can be easily derived in spherical coordinates, as indicated by the geometry in Fig.3. The cone model number was 40.

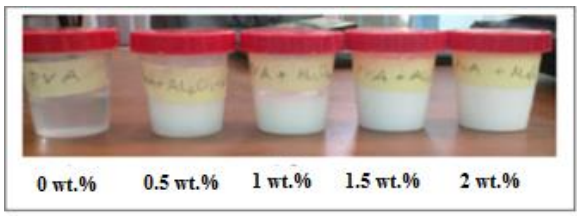


Fig. 2 Samples of PVA/nanoparticles Al_2O_3 solutions.

Fig. 3: Glove box used for mix Al_2O_3 NPs with PVA solution.

Fig. 4: Rheometer Cone on plate.

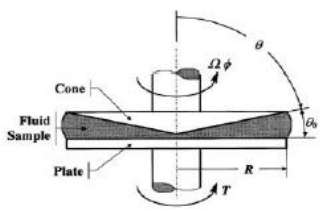


Fig.5:Cone plate viscometer geometry.

Atomic Force Microscope: Atomic Force Microscopy (AFM) version AA3000 was used to check the surface topography, roughness, distribution of NPs and its agglomeration through the matrix. A small piece of polyvinyl alcohol Nano composite film at 0.5, 1, 1.5 and 2 wt.% of Al_2O_3 NPs are prepared for this test.

pH Meter: pH measurements of solution Samples were measured by using inoLapPh. 720 supply by "WTW", at room temperature 25c°.

Density Device: The density resylts were obtained by using "Matsuhaku". the liquid density mode of GP-120s instrument. The temperature selected for determining the specific gravity was 25C°.

Tensiometer: The surface tension was tested using JZYW-200B Automatic Interface Tensiometer supply by "BEING UNITED TEST CO., LTD." By using direct methods measuring the force required to pull, for instance, a metal ring out of a liquid at 25 C°.

FTIR Spectroscope: The FTIR spectra in absorption mode were recorded on a Bruker Optics Vertex 70. After evaporation of solute, PVA and PVA/Al_2O_3 NPs composites films as well as Al_2O_3 NPs were tested in the region from 500 to 4000 cm^{-1}.

Results and Discussion

Viscosity: The Effect of Al_2O_3 Nanoparticles Percentage on solution viscosity of polyvinyl alcohol has been illustrated in figure 6. It shows a dramatic decrease in viscosity of the PVA solution with shifting NPs. This occurs because interaction between NPs and polymer chains, which introduce lubricant factors, lead to less friction around molecules as well as between NPs. In more detail, In low proportion of about 0.5-1 wt.%, there is obviously a sharp drop due to interchanging the particles inside polymer chains to make lubrication. But in high content for additives there are stable states in flow behaviour because all the spaces between molecules of polymer had been filled with Al_2O_3 NPs. Therefore, interaction between particle-to-particle ratio become more than the particle-to-chain ratio.

To hypothesize, if another concentration is added to the solution, for example 3-4 wt.%, the viscosity will increase gradually and become act as a shear thickening-like behaviour. In other words, the best ratio of Al_2O_3 NPs content is founded around 1 wt.%.

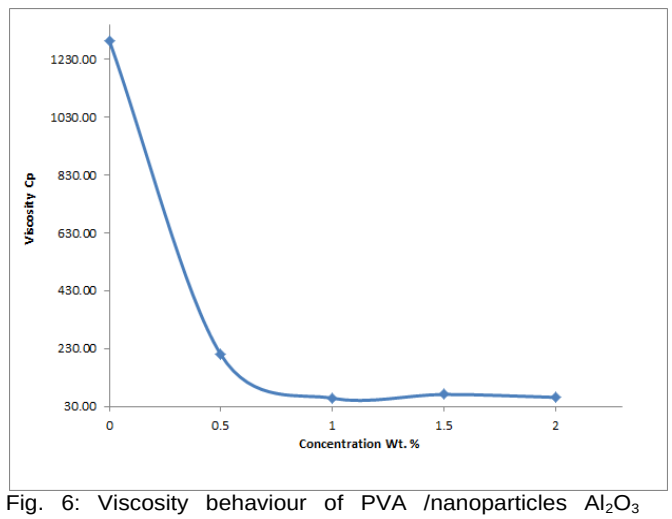


Fig. 6: Viscosity behaviour of PVA /nanoparticles Al_2O_3 solution at different concentrations.

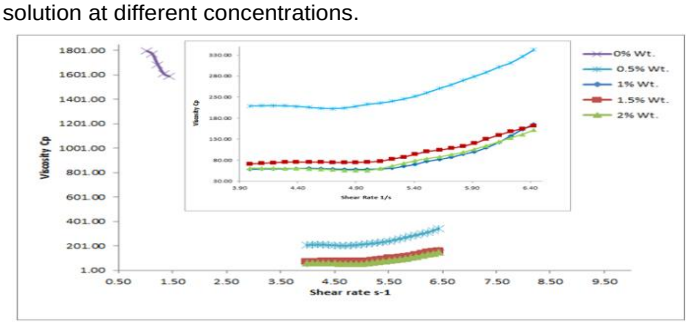


Fig. 7: viscosity - shear rate behaviour of PVA /nanoparticles Al_2O_3 solution at different concentrations.

Viscosity-to-shear rate relationship of PVA/Al2O3 NPs solutions at different concentrations has been reported in the diagram below Figure 7. It appears clearly shear thinning behaviour in a pure PVA sample, that may be attributed to polymer chains disentanglements, while there are two stages flow manner produced by mixing Al_2O_3 NPs into the PVA solution. With respect to high interaction between functional groups on polymer chains and Al_2O_3 surfaces, NPs take place between polymer molecules to make two different rheological characteristics depending on the movement period. In the first, when there is low shear rate, there is much time available to occupy free volume places by particles, therefore Newtonian and semi stable flow shapes have recorded generally. But increasing the shear rate leads to low periods to permit the NPs to move and transfer inside the polymer solution. That makes many agglomerations and high friction forces to encourage shear thickening fluid properties, in the second stage.

Experimental data for shear stress of PVA/Al_2O_3 NPs against shear rate have been plotted in figure 8 at different concentrations. In pure sample, the PVA solution traditionally have Shear thinning behaviour and fits to standard characteristics for shear thinning except last point appear out model. Increasing in shear rate reduce polymer chains entanglements and encourage chains sliding, so shear stress decrease with shear rate. On the other hand, using Al_2O_3 NPs turn off behaviour towards Newtonian flow at the began. This is as result to lubricant effect of Al_2O_3 between chains until identify level of about 4.75 s-1 depending on ratio of the free volume founded between polymer chains to NPs speed, as well as NPs dispersion level inside solution. Secondly, thebehaviour become as shear thickening manner with shear stress increasing. Many Factors may be having rule in that, one of them, high shear rate does not permit sufficient time for molecules to move around them, also in progressive there are attractive forces crated between functional groups on partials surfaces to make attraction force inside NPs more in general. This behaviour is similar approach founded in viscosity-shear rate relationship.

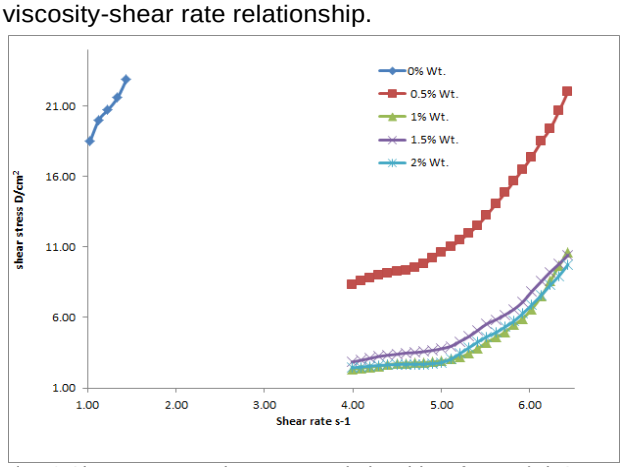


Fig. 8:Shear stress- shear rate relationship of PVA/Al_2O_3 NPs solutions at different Al_2O_3 NPs concentrations.

Determination of Rheological Model: The shear stress - shear rate characteristic analysis of all samples are tabulated in Table 1 below to show Bingham, Casson, NCA/CMA Casson, Power Law, IPC Paste and Herschel Bulkley models analysis of the flow curves that had been achieved using Rheocalc program. In Bingham model analysis, the values indicate little approach between exponential data and fitting values, only in very low concentration around 0.5 wt.% that is about 99.2-91.2% of fits confidence, this may be because of Bingham model uses to describe linear relationship with plastic viscosity behaviour. While Casson, NCA/CMA Casson and Herschel–Bulkley models' analysis are displayed interesting relationship of tested to real values, because induce nonlinear relationship which nearly of complex polymer structure. On the other hand, power law and IPC Paste model's analysis cover moderate correlation in comparison state of them, as result to lack of plastic viscosity as yield stress. However, Herschel–Bulkley model fitted satisfactorily the experimental data with the correlation coefficient higher than 98% in all cases, because of it have two characteristics factors to describes the flow behaviour more generalized, especially for polymer chains structure. Accordingly, it represents the best model to mention the flow behaviour of PVA/Al_2O_3 NPs, and we will discuss this model analysis in more deeply view, which also may be used to describe the connection of tests in liquid and solid states, respectively. Figure 9-B, illustrated the closer sample was founded to fit Herschel–Bulkley model is 0.5 wt.%, while in the figure 9-A, the faraway sample was appeared with 98.3% in the state pure PVA, therefore, additive NPs makes higher fitting approach to Herschel–Bulkley model. Additionally, it is appeared not full fitting in analysis with theincrease concentration of NPs. In other words, decrease of confidence fit value of Herschel–Bulkley model analysis from 99.9% at 0.5 wt.% of NPs as in figure 9B to 99.4% at 2 wt.% as in figure 9E, while it was 98.3% for pure sample of PVA as in figure 9A.

$$\tau = \tau_0 + K\gamma^n \quad (1)$$

In equation (1), that represents Herschel–Bulkley model, τ and τ_0 refer to the shear stress and yield stress, respectively, the latter of which is a critical value of shear stress, below which a plastic material behaves like a solid. k and n represent the fluid consistency and fluid behaviour index, respectively, and γ signifies the applied shear rate.

In figure 9, the flow behaviour of pure PVA have index value less than 1, about 0.18, so it acts as a shear thinning behaviour. While, using of NPs as additives for PVA polymer lead to flow index values higher than 1, for example at 0.5 wt.% equals to 6.10, which represent the lowest value of flow index. Therefore, the flow turns of the manner toward shear thickening behaviour. Moreover, the high flow index number has been founded around 10.2 at 1 wt.%, so that the best result is founded to act as shear thickening behaviour about 1 wt.% and this

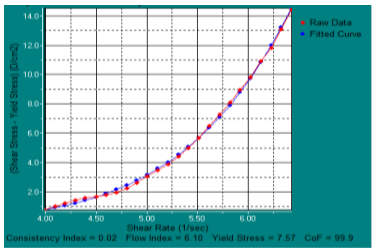
concordance with viscosity – concentration measurements that was illustrated in figure 6.

Table 1:Curve fits confidence values by using a Rheocalc program for different models.

Model	Concentration wt.%				
	0	0.5%	1%	1.5%	2%
Bingham	99.2	91.2	76.2	85	79.4
Casson	99.6	96.2	90.9	94.1	91.9
NCA/CMA	99.6	96.2	90.9	94.1	91.9
Power lae	99.2	93.4	85.3	90.5	86.8
IPC paste	99.2	93.4	85.3	90.5	86.8
Herschell Bulklev	98.3	99.9	99.8	99.7	99.4

A

B



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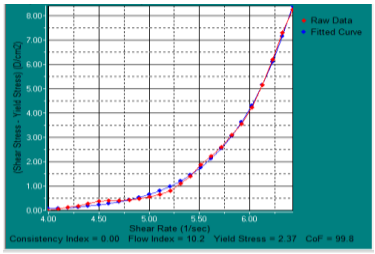

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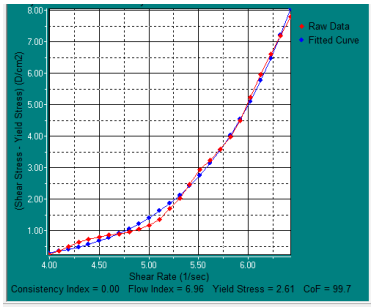

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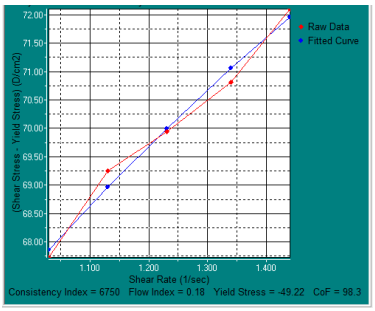


Fig. 9: Herschel-Bulkley Model analysis by sing Rheocalc program of PVA/Al_2O_3 NPs solution at different concentrations (A= 0 wt.%, B=0.5 wt.%, C= 1 wt.%, D= 1.5 wt.% and E= 2 wt.%).

Density: It is generally accepted that, when mix high density materials with another materials which have less density, it will increase, due to mixing rule, but in nanoscale this is sometimes have differently results. Such as in our work that shown in figure 10, the density of PVA/Al_2O_3 NPs solutions decreases slightly with the Al_2O_3 NPs concentration increasing. This is may be attributed to the free volume effect introduced by inter the Al_2O_3 NPs between polymer chainsand produce exclusion among them. Therefore, density results correspond the viscosity flow behaviour of PVA/Al_2O_3 NPs solutions that was founded to decreases with Al_2O_3 NPs loading, on account of the free volume effect mechanism.Moreover, it is clearly appearing in figure 10, there are high drop down of the density in low NPs content around 0.5-1 wt.%, as result of high ability to distribution between polymer chains to encourage the free volume, so it given better reduction in viscosity behaviour. However, there are approximately constancy in density outcome between 1-2 wt.%, because of repletion the free volume between polymer chains with NPs. In other words, the free volume effect mechanism works in lower content of NPs and it represent better effect to reduction the viscosity of PVA solution.

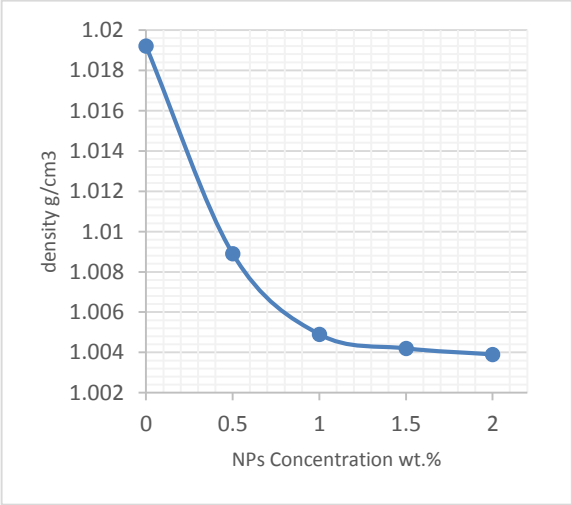


Fig. 10: Density behavior of PVA/Al_2O_3 NPs solutions with Nano concentration increasing.

Surface tension: As is shown in the figure 11, , the surface tension of PVA/Al_2O_3 NPs solutions were plotted with regard Al_2O_3 NPs percentage increasing. The shape states clear decreasing of surface tension with Al_2O_3 NPs increment except the first percentage of about 0.5 wt.%. This diminution especially at concentration of about 1-2 wt.% attributed to high dispersion Susceptibility of Al_2O_3 NPs inside PVA solution to make attraction forces. Therefore, the adhesive forces between oxygen atoms that was founded on surfaces of Al_2O_3 NPs andhydroxyl groups of PVA chains are more than cohesive forces of them between Al_2O_3 NPs or PVA chains, respectively. In other words, the internal forces smaller than external forces. As well as, the number and ratio of adhesive forces are high as a result to high surface area of NPs, otherwise, this effect produces the forces distribution that lead to the plasticizing effect mechanism. The stable state of surface tension at 0.5 wt.% may be attributed to balance forces that happened because the PVA chains covering the Al_2O_3 NPs is not in full station. Therefore, the decrease in the viscosity at first percentage is not indicator of the plasticizing effect mechanism.

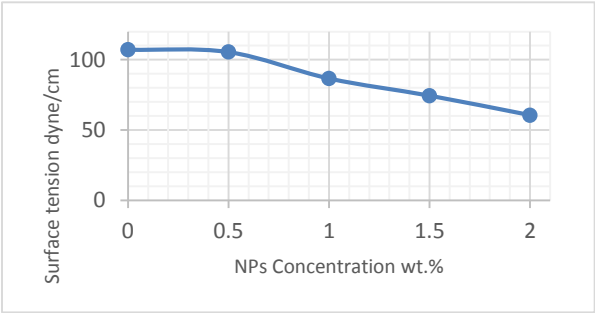


Fig. 11: Surface tension behavior of PVA/Al_2O_3 NPs solutions with Nano concentration increasing..

pH Measurements: To understand the role of the 'selective adsorption' mechanism in flow behaviour of the PVA solution viscosity, pH meter was used. Figure 12 shows the pH number of PVA/Al_2O_3 NPs solutions at different content of Al_2O_3 NPs wt.%. The pH number increases with the Al_2O_3 NPs concentration increasing from 7.9 to 8.5, due to high content of hydrogen atoms in PVA backbone and H_2O molecules with respect to lower amounts of oxygen atoms in it. Besides that, the lower ability of AL to interact with only oxygen atoms while higher for oxygen to attraction with hydrogen atoms. Therefore, high freedom amounts of OH^- ions in the solution are resulted to make pH number decrease with every AL and oxygen additions by Al_2O_3 NPs loading. However, at low pH number the NPs have a positive surface charge while at high pH there is a negative surface charge. The isoelectric point is the intermediate pH in which the NPs surface has zero net surface charge. The measured isoelectric point for Al_2O_3 NPs is approximately 7.0, so that the particles have a positive zeta potential when pH is lower than 7, while the zeta potential is negative when the pH number is higher than 7.

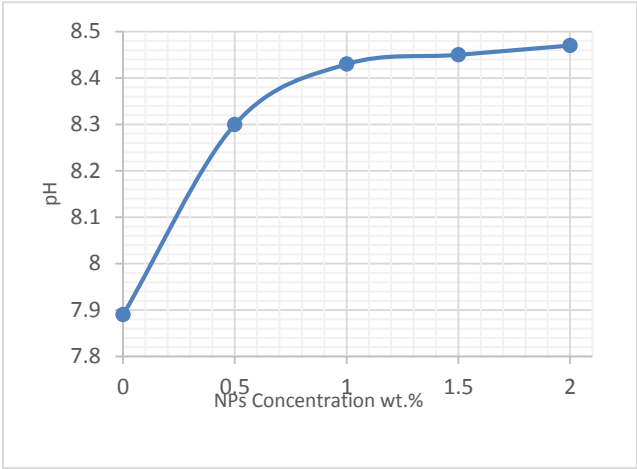


Fig.12: pH number of PVA/Al_2O_3 NPs solutions at different concentrations of NPs.

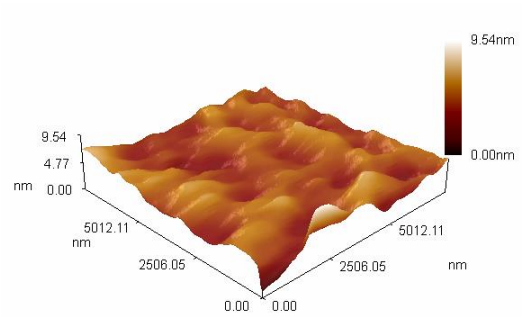
In addition to that, when pH number is far from the isoelectric point, 7.9 in pure PVA solution into 8.5 of PVA/Al_2O_3 NPs solution at 2 NPs wt.%, the absolute value of zeta potential becomes higher. Moreover, the electrostatic repulsive force is then dominant over the van der Waals force lead to suppressed the Al_2O_3 NPs agglomerations. Otherwise,the 'selective adsorption' mechanism have biggest effect on the viscosity reduction in high concentration of NPs, but in fact with our research, there is little indicator for this mechanism to understand and explain the viscosity flow behaviour manner and which approve by semi stable of pH number especially in high percentage. As well as, the results of viscosity are semi stable in high loading of Al_2O_3 NPs as it is showed in figure 6.

Surface topography of sold samples: After evaporated the solute, Surface topography of PVA/Al_2O_3 NPs composites have been studied by atomic force microscopy (AFM) to understand Al_2O_3 NPs distribution, which effected on the flow behaviour of the solution as well as the molten state. Figure 13 shows three-dimension (3D) surface layer of the nanocomposite's samples with the changing Al_2O_3 NPs concentration.

Also, the surface roughness of samples was sitting in figure 14 with regarded the increasing percentage of Al_2O_3 NPs. Due to 3D image, It is obviously that there are significant dispersion of Al_2O_3 NPs inside PVA polymer molecules, especially at percentage between 0.5-1 wt.% NPs, which permit disentanglement of polymer chains during the solution movement, so the viscosity was reduced because of the 'ball-bearing' effect mechanism. Where, NPs takes the places between the PVA chains as ball bearing phenomena to encourage friction reduction [25]. Therefore, the surface roughness sharply drops down with NPs content increasing at all samples with respect to the pure PVA, especially at 0.5-1 wt.%.

On the other hand, in progressive another additive of Al_2O_3 NPs lead to NPs semi-agglomerations between PVA polymer chains to identify level as shown in figure 13D and 13E, which are resulted in steady state of viscosity measurements that was showed in figures 6,7 and 8. This may be attributed to overcome high content of NPs in composite and distance lost between molecules to work as ball bearing joint, overall. Furthermore, the surface roughness begins to grow up with regard to 0.5 wt.% as a result of Al_2O_3 NPs agglomerations groups inside matrix. The stable-like state of surfaces roughness at about 1-2 wt.% of Al_2O_3 NPs in figure 14 are happened due to semi-full stage of spaces inside polymer molecules, as well as, a result to decreasing the free volume which is showed at figure 10, that responsible on diffusion and dispersion of NPs into polymer matrix.

A



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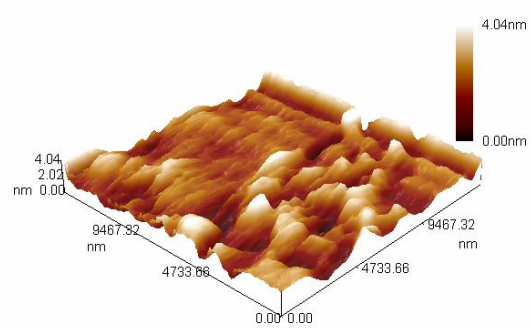

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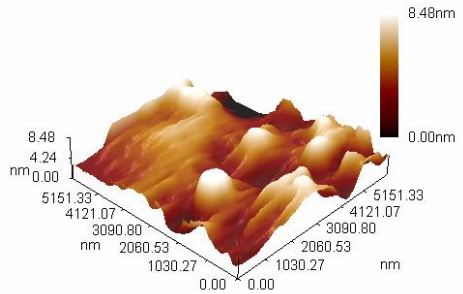
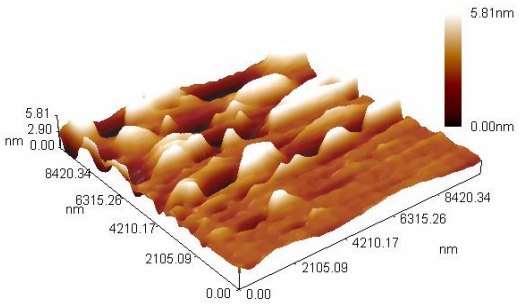


D



E

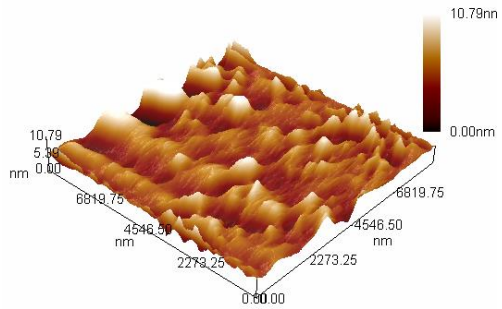


Fig. 13: Surface topography of Al_2O_3Nano.PVA composite at different concentrations; (A=0, B=0.5, C=1, D=1.5, E=2 wt.5%) by AFM.

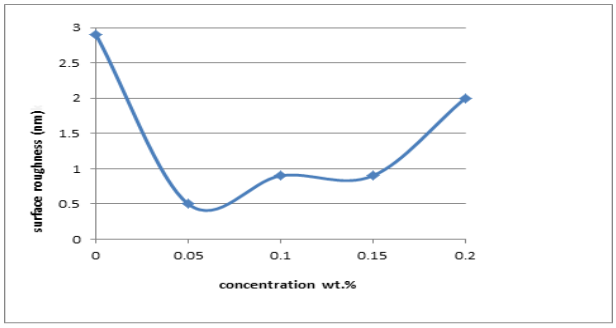


Fig. 14: Surface roughness of Al_2O_3Nano.PVA composite at different concentrations by AFM.

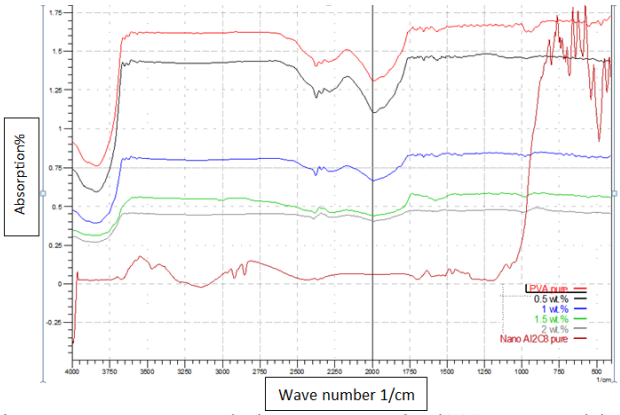


Fig. 15: FT-IR transmission spectra of Al2O3 nanoparticle, poly(vinyl alcohol), poly(vinyl alcohol)/Al2O3 Nano composites.

However, with respect to higher concentration, such as 2 wt.% in figure 13E the topography behaviour and the surface roughness in figure 14, are developed to become more valuable. So that, shearthickening behaviour were introduced in Rheological characterizes of PVA/Al_2O_3 NPs solutions that were showed in figures 7 and 8. In summary, there are high connection and matching between values of surface topography and roughness of solid samples to that related to solution properties, such as viscosity/shear rate/shear stress relationship and density measurements. Therefore, the 'ball-bearing' effect mechanism have good approach to describe and explain the flow behaviour of PVA/Al_2O_3 NPs**.**

Fourier-Transform Infrared Spectra (FTIR): In addition to pH meter test, FTIR spectroscope test was used to check the effect of the 'selective adsorption' mechanism on flow behaviour of PVA/Al_2O_3 NPs solutions, to known the interactions and attractions between particles, chains, molecules and atoms. However, the IR spectra in absorption mode which was performed over the region 500–4000 cm-1 of PVA, Al_2O_3 NPs and PVA/Al_2O_3 NPs composites are showed in figure 15. In pure PVA, broad peak between 3600 cm^{-1} and 3000 cm^{-1} with precise peak appear at 3620 cm^{-1} assigned to the free O-H vibration in PVA. Also, interesting peak observed at 1060 cm^{-1} and 880 cm^{-1} assigned to the C-C stretching and C-H rocking of PVA. Besides that, the band peak presence at 1490 cm^{-1} belongs to C-H bend of CH2 in PVA [28]. Also, the IR spectrum of Al_2O_3 NPs is represented by many clear bands and the most important of them are located between 1000 cm^{-1} and 400 cm^{-1}, because there are high absorptions of them to infrared waves. A comparison of IR spectra of the PVA pure, Al_2O_3 NPs and PVA/Al_2O_3 NPs composites revealed decrease in the intensity ratio of bands at 1100, 1743, 2167 cm^{-1} and broad band between 2644-3860 cm^{-1} independently with the concentration of Al_2O_3 NPs implies the existence of a decoupling process between O–H plane vibrations and C–H wagging vibrations, that may be due to interaction between the Al_2O_3 NPs and the OH groups attached to the backbone of PVA chains.

Moreover, the most distinct feature in the FTIR spectra of the PVA/Al_2O_3 NPs composites was the appearance of the absorption band at around 940 cm^{-1}. Taking into account the presence of oxygen molecules on the surface of the Al_2O_3 NPs, the possibility of hydrogen bond formation between them and hydroxyl groups from the polymer chains could be an explanation for the increase in intensity of absorption and appearance of the band at 940 cm^{-1}. The existence of such functionality within PVA chain imparts additional binding locations for Al_2O_3 NPs. As well as, the presence of Al_2O_3 bands, such as 940 cm^{-1} in the IR spectrum of PVA/Al_2O_3 NPs composites confirms the incorporation in physical attraction of the NPs into the polymer matrix, which plays important rule for the 'selective adsorption' mechanism. These resultssuggest that the Al_2O_3 NPs effectively interact with the PVA chains, affecting their vibrational modes and, therefore, their rheological and topographical properties.

The intensity of the interaction between a polymer chains and Al_2O_3NPs critically depends on the content of NPs, i.e., the inter-particle distance. In order to reveal the possible chemical attraction between the Al_2O_3 NPs and the PVA matrix, therefore, the slight decrease in the intensity of bands in the PVA/Al_2O_3NPs composites samples with increasing the NPs content compared to the PVA pure was founded.

CONCLUSIONS

The viscosity of PVA/Al_2O_3 NPs decreases rapidly at specific concentration, (0.5% wt), then remains stable up to higher ratios. All viscosity samples increase with the shear rate escalating after 5 s^{-1}, with Newtonian flow obtained prior to that. Therefore, a certain concentration and the shear rate were important parameters to characterize the NPs for their application. The shear thickening behaviour at high shear rate attributed to the interactions between the function groups and the NPs. This phenomenon can be enhanced by controlling the NPs and polymer ratio. However, this behaviour increases viscosity with shear rate while it decreases with concentration, and can be used as a novel method to control viscosity. In other words, increasing Al_2O_3 NPs loading in the solution caused steady viscosity to decreases to different degree, while increasing the shear rate leads to the viscosity increasing. Therefore, it is sufficient method to control the PVA viscosity for different ranges by using these two factors - shear rate and concentration. Density and pH tests explained the physical changes associated with the viscosity behaviour. While AFM and FTIR tests enter the structures to discover the topography and chemical variations related to the flow behaviour. The results show the best mechanisms that works together to explain the flow behaviour of PVA/Al2O3 NPs solutions are the free volume effect and the ball-bearing mechanisms. In addition, the data are fitted to mathematical standard models to know which model most closely resembles the experimental results. The flow behaviour analysis of PVA/Al_2O_3 NPs solutions showed performance properties highly matched the Herschel–Bulkley fluid model.

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