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Effect of Titanium Dioxide Nanoparticles (TiO_2 NPs) on Rheological Characteristics Behavior of Poly Vinyl Acetate (PVAc)

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Abstract

Rheological properties investigation of polymer solution with inorganic nanoparticles aqueous mixtures were studied. In the present work, Polyvinyl Acetate (PVAc) was used in a form aqueous solution, while titanium dioxide nanoparticles (TiO_2) was used as an inorganic additive. PVAc was loaded with 0, 0.5, 1, 2, 3, and 4 weight percent (wt. %) of TiO_2 nanoparticles, where the maximum concentration of TiO_2 was 4 wt. % that gives the enough information about the behaviour. Cone on plate Rheometer was applied to measure rheological characteristics of PVAc/TiO_2 mixture flow at different shear rates, while Tensometer, pH meter, and Densitometer were used to peer understanding of flow mechanisms. The results were shown a significant change in shear stress-shear rate behavior with the TiO_2 ratio increasing, especially at 2-3 wt. %. The shear stress decreasing with the shear rate increases. The viscosity tends to decrease with the high shear rate values about 1.14-1.3 s-1 in low concentration of TiO_2 nanoparticles about 0.5 wt. %. The pH and surface tension values show an interesting decreasing overall range of PVAc/TiO_2 nanoparticles. These results have an important effect on processing and capability production in polymer composites technology, as well as energy conception in polymer and composite technology of PVAc/TiO_2 nanoparticles composite.

Keywords

Polyvinyl Acetate, Titanium dioxide nanoparticles, Rheological properties, Fluid flow, Cone on plate

Introduction

The rheological properties of polymer solution are important factors in many stages of industrial production, for example in adhesives, bio nanofibers in the electrospinning process, and in painting industries. This is because it has effects on the economical, structural and final features of polymer products [1, 2]. Poly (vinyl acetate) (PVAc) is low cost and has acceptable mechanical and thermal properties, high functionalities, biodegradability, biocompatibility [3, 4]. Therefore, it has been used in a wide range of applications such as adhesives, bio nanofibers in electrospinning, and in painting industries [5].

In recent years, PVAc has mixed with inorganic bio nanoparticles, such as nano clay, starch, cellulose nanofibrils, SiO_2, TiO_2, to produce bio nanofibers in electrospinning process for many biomedical applications. The chemical, mechanical and biomedical characterization of that final composites have been studied [6-9]. However, there is a lack of rheological and flow characteristics studies of these applications. Another important property of PVAc is an adhesive property that can be modified by adding various nanoparticles to reduce the weaknesses of adhesives ability, which may affect the flow properties during the manufacturing and in the final product [10-12]. Petrasa et al., studied the viscosity of PVAc that uses in nanofiber industries for biomedical and industrial applications [13]. Ferreira et al. pointed out PVAc has a weakness against UV when it applied in decorative, especially outside home applications [14]. Lianga et al. presented the application of PVAc in painting and how its viscosity measurements and values effect on the painting quality and properties [15].

Titanium dioxide (TiO_2) is one of the most important inorganic bio nanoparticles that has a wide range of applications in polymer engineering process [4]. It has characteristics such as inexpensiveness, nontoxicity, good photostability, UV resistivity, and high reactivity [17]. Tankut et al., investigated the effect of TiO_2 nanoparticles on the mechanical bonding strength of PVAc adhesive, which was improved at open-time of 5 and 10 minutes as TiO_2 nanoparticles were added [18]. Bardak et al., determined the bonding strength and structural properties of the composites that prepared with PVAc and nano TiO_2 fillers at different loading rates (1%, 2%, and 4%) [19]. The results showed there are enhancement tin the bonding strength and

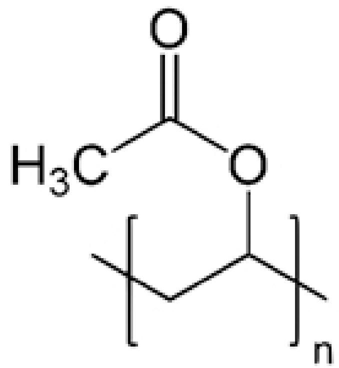

Figure 1: Chemical structure schematic of PVAc [20].

structural properties of the produced composites. However, the flow characteristics have not taken into account, which may play a significant role in the processing and final stages of production. In this work, the effect of inorganic nanoparticles (TiO_2) on rheological properties and flow behavior of polymeric solutions (PVAc) viscosity were evaluated at different concentrations, shear rate and shear stress. Also, other properties such as density, surface tension and pH meter were used to predict and understand the viscosity behavior more deeply.

Experimental

Materials

All materials were used as it obtained without any further purification or modification, where polyvinyl acetate (PVAc) was supplied in solution form by Changzhou haijian new textile materials CO.LTD/china. Also, Titanium dioxide nanoparticles (TiO_2 NPs), CAS number: 13463-67-7 with high purity ≥ 99% was supplied in nanopowder form by Shanghai Yuefang Industry & Trade Development Co., Ltd. Shanghai, China.

Samples preparation

At the first, PVAc solution was weighted to a specific amount, then TiO_2 NPs of 0, 0.5, 1, 2, 3, and 4 weight percent (wt.) of TiO_2 NPs were added into the PVAc solution by using glovebox facility for safety. Before TiO_2 NPs added, it had been dried for 5 minutes in oven temperature 100 °C to remove any humidity on NPs surfaces and to achieve better dispersion and interaction between NPs and polymer. Then, mixtures were mixed using a magnetic stirrer for 30 minutes with heating at about 70 °C before rheological characterization was applied, as shown in figures 2 and 3.

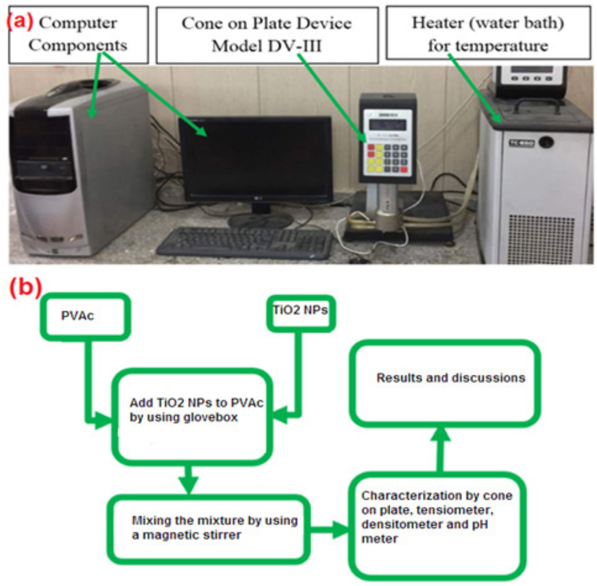

Figure 2: (a) Rheometer Cone on Plate Model DV-III, (b) Study plan of experimental procedure steps.

Equipment

The flow behavior was studied by using Brookfield cone on plate viscometer device found in polymers laboratories in the University of Babylon, as shown in figure 2a. The simple cone-and-plate viscometer geometry provides a uniform rate of shear and direct measurements of the first normal stress difference. It is the most popular instrument for the measurement of non-Newtonian fluid properties. The cone model number was 40. So, the sample volume was 2ml [21]. The density measurements were obtained by using Matsuhaku the liquid density mode of GP-120s instrument found in Polymers laboratories at the University of Babylon. The temperature selected for determining the specific gravity was 25°C. The surface tension was tested using the JZYW-200B Automatic Interface Tensiometer supply by Being United Test CO., LTD." in the chemistry laboratory, by the direct method that measures the force required to pull, for instance, a metal ring out of a liquid at 25 C. pH samples were measured by using inoLapPh. 720 that supply by "WTW" in the chemistry laboratory.

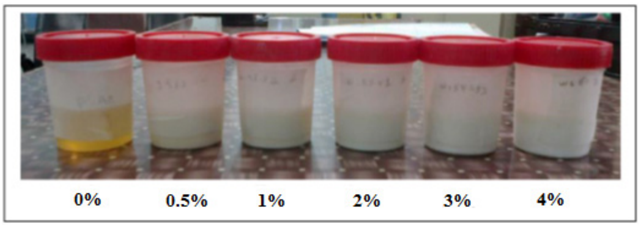

Figure 3: Samples of PAVc/TiO_2 nanoparticles solutions.

Results and Discussion

Figure 4 shows the relationship between viscosity behavior and TiO_2 nanoparticles concentration of PVAc/TiO_2 mixtures at different shear rates. It is clear that there is interesting change in the behavior of flow viscosity from shear thinning at low shear rate into shear thickening behavior at high shear rate. Generally, the viscosity increases with TiO_2 nanoparticles loading, except in low shear rate and high ratio of TiO_2 nanoparticles, (0.67 – 0.82) s-1, (0-1) wt. %, respectively. This viscosity decreasing behavior may be attribute to high ability for tiny TiO_2 nanoparticles to dispersion in solution in suitable time at low concentration. The low shear rate permit for nanoparticles to locate the free volume and disperse between polymer chains, while the low concentration introduces fitness the free volume between chains to nanoparticles movements [22]. The increasing in viscosity could be belong for the agglomeration of TiO_2 nanoparticles between the chains of PVAc into micron size as a result of high concentration as well as unsuitable dispersion time. This behavior increases the friction between the chains led to high viscosity. In other words, the high concentration of nanoparticles encourages high probability to contact particle to particle than particle to polymer chain [23].

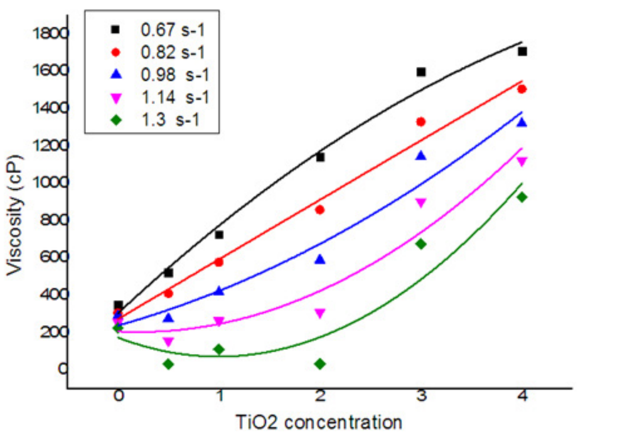

Figure 4: Viscosity behavior of PVAc/TiO2 with different ratios of TiO2 nano particles with regard to change of shear rate.

The curve of the relationship between viscosity and shear rate was shown in figure 5. It seems that the viscosity decreases with shear rate increases slightly in pure sample, while it behaves in sharp manner with increasing TiO_2 nanoparticles concentration. This changing in behavior may be due to an increase in the disentanglement between nanoparticles and chains, which increase the degree of this phenomenon that called shear thinning effect. These behaviors of decreasing viscosity with shear rate and increasing it with concentration can be a powerful factor to control polymers viscosity in processing [24]. As result of that, the energy consumption and product quality can be achieved by applied TiO_2 NPs in polymers technology, especially with PVAc.

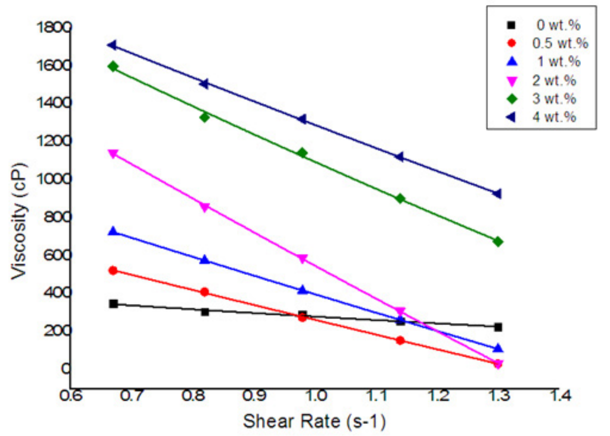

Figure 5: Viscosity behavior of PVAc/TiO_2 with different ratios of TiO_2 nanoparticles.

The shear stress - shear rate relationship with different ratios of TiO_2 nanoparticles have been illustrated in figure 6. This figure shows a significant decreasing behavior of shear stress with shear rate increasing at TiO_2 nanoparticles loading between 1 and 3 wt. %. While the shear stress increasing with shear rate in pure sample as well as in very low and high loading of TiO_2 nanoparticles, 0, 0.5, 4 wt. %, respectively. The decrease in the shear stress in 4 wt. % could be as a result to the sufficient dispersion and high lubricant ability of TiO_2 nanoparticles between polymers chains [25]. This decreasing in shear stress leads to save consumption energy in polymer processing technology.

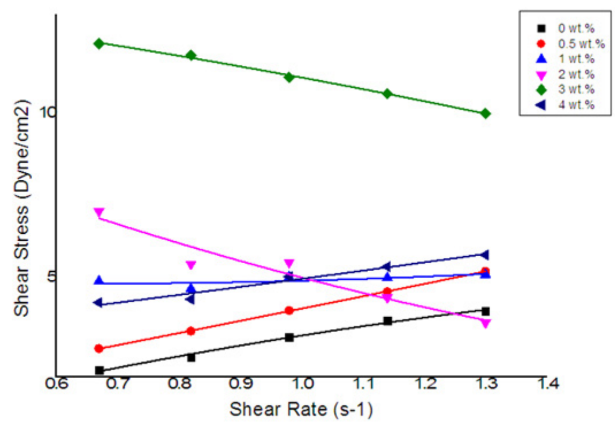

Figure 6: Shear stress – shear rate behavior of PVAc/TiO_2 with different ratios of TiO_2 nano particles.

Behavior of viscosity - shear stress was plotted in figure 7. The curve shows different behaviors, in the samples with loadings of 0, 0.5, and 4 were behaves in decreasing manner, while for concentration of 1, 2, and 3 were represented increasing flow manner. That is behavior was due to the high differences in degree of dispersion of TiO_2 nanoparticles [26].

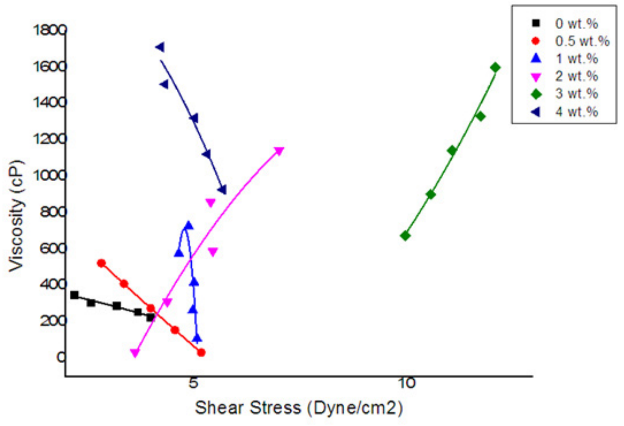

Figure 7: Viscosity behavior of PVAc/TiO_2 with different ratios of TiO_2 nano particles with regard to change of shear stress.

The surface tension and pH report of PVAc/TiO_2 nanoparticles at different ratios of TiO_2 is represented in figure 8. It is clear that the surface tension decreases with content loading of TiO_2, due to the dispersion of TiO_2 nanoparticles inside PVAc solution. In other words, the adhesive forces between TiO_2 nanoparticles and chains are more than cohesive forces between TiO_2 nanoparticles itself, which is mean the external force greater than internal force. The stabilization ability techniques which include cohesive and adhesive forces play an important role in dispersion and agglomeration nanoparticles inside polymer solutions [27].

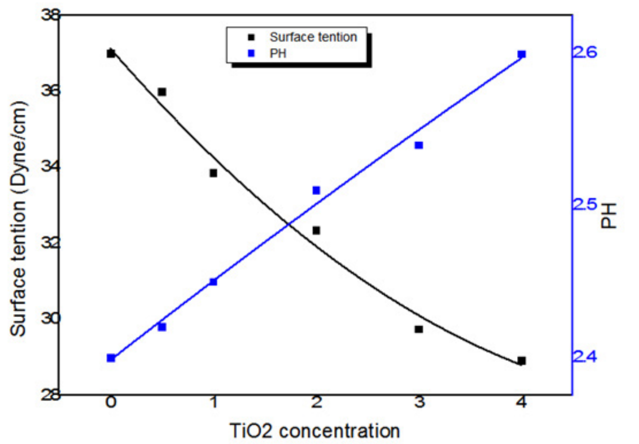

Figure 8: Surface tension of PVAc/TiO_2 with different ratios of TiO_2 nanO particles with regard to change of shear rate.

In addition to that, the pH value increases with the increasing of TiO_2 concentration. The isoelectric point is the intermediate pH, the particle has zero net surface charge. The measured isoelectric point for TiO_2 is approximately 6.0. the Particles have a positive zeta potential when pH is lower than 6, while the zeta potential is negative when pH is higher than 6. However, when pH is approaches from the isoelectric point (increase from 2.4 to 2.6), the repulsive force is weakened due to low surface charge, and the hydrodynamic size increases beyond which it is measurable. Moreover, pH tends to near values of 7, so there are good polar bonds between TiO_2 and polymer chains and then good dispersion.

The density report of PVAc/TiO_2 nanoparticles at different loading of TiO_2 have been shown in figure 9. The curve illustrates there is increasing on density with TiO2 concentration increasing, that is may be as a result to the rule of mixtures, where TiO_2 nanoparticles are agglomeration to micron size and TiO_2 have high density (high from PVAc) [22]. Density report was increasing in low concentration of NPs, while tend to semi stable with high loading. That is matching surface tension and pH measurements curves as well as viscosity – concentration relationship behavior. Density behavior looks in semi stable due to saturation and decreasing in free volumes between polymer chains with TiO_2 [27].

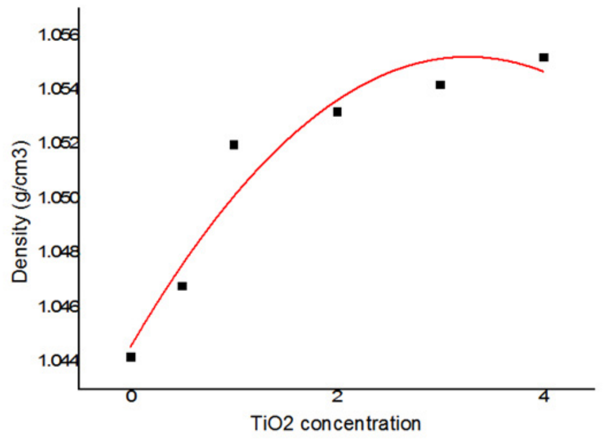

Figure 9: Density measurements of PVAc/TiO_2 with different ratios of TiO_2 nano particles.

Conclusions

Rheological properties investigation of polymer solution/ inorganic nanoparticles aqueous mixtures show interesting effect for using TiO_2 nanoparticles on polymer rheology. Poly vinyl acetate (PVAc) is used in this work in form aqueous solution, while titanium dioxide nanoparticles (TiO_2) was used as inorganic additive. PVAc was loaded with 0, 0.5, 1, 2, 3 and 4 weight percent of TiO_2 nanoparticles. Cone on plate Rheometer was applied to measure rheological characteristics of PVAc/TiO_2 mixture flow at different shear rates, while Tensometer, pH meter and Densometer were used to peer understanding of flow mechanisms. The results were shown significant change in shear stress-shear rate behavior with TiO_2 ratio increasing, especially at 2-3 wt. %. The shear stress decreasing with shear rate increasing. In low content of TiO_2, about 0.5 wt. %, and in high shear rate, the viscosity tend to decreases with shear rate and TiO_2 concentration. The pH and surface tension values show interesting decreasing over all range of PVAc/TiO_2 nanoparticles. These results have important effect on processing and capability, as well as energy conception in polymer and composite technology of PVAc/TiO_2 nanoparticles composite. Also, application this nanocomposte films processing which is used as UV-masks for various applications and as anti-reflection coatings in solar cells (PVAc/TiO_2) nanocomposite films with enhanced visible-light photocatalytic activity.

Conflict of Interest

The authors declare no conflict of interest.

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