

Rheological behavior of starch-poly(vinyl alcohol)-TiO₂ nanofluids and their main and interactive effects

Saeed Mousazadeh,¹ Abolfazl Shakouri,^{1,2,3} Mohammad Hojjat,² Seyed Gholamreza Etemad,⁴ Saeed Zeinali Heris³

¹Department of Chemical Engineering, Quchan Branch, Islamic Azad University, Quchan, Iran

²Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29201

³Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

⁴Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran

Correspondence to: A. Shakouri (E-mail: shakouri@mailbox.sc.edu; shakouri@live.com)

ABSTRACT: In this study, an investigation of the rheological behavior of starch/poly(vinyl alcohol) (PVA)/titanium oxide (TiO₂) nanofluids was performed. It revealed that the rheological behavior of starch suspensions displays a particular change due to the presence of PVA and TiO₂. All examined fluids demonstrated non-Newtonian behavior and followed the Power law model. The main and interacting effects of starch, PVA, and TiO₂ nanoparticles concentrations were studied using the analysis of variance. The results indicated that the flow behavior index (n), as well as the consistency index (K) of suspensions, is influenced by the PVA and TiO₂ contents. The flow behavior index (n) decreased and consistency index (K) increased by an increase in PVA concentration. A reverse trend is observed by the addition of TiO₂ nanoparticles to starch and PVA blend suspensions. The difference in rheological behaviors was ascribed to the presence of binary and triplet interactions between starch, PVA, and TiO₂ nanoparticles. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44062.

KEYWORDS: colloids; nanoparticles; nanowires and nanocrystals; rheology; viscosity and viscoelasticity

Received 25 February 2016; accepted 6 June 2016

DOI: 10.1002/app.44062

INTRODUCTION

The use of starch has been implemented in industrial applications due to its biocompatibility, low cost, and wide availability. Aqueous suspension of starch has great technological importance in many applications, including cosmetics, pharmaceuticals, fertilizers, papermaking and paper-related products, adhesives, textiles, coatings (wood and metal), oil-well drilling, and bioplastics.¹ Awareness of the rheological properties of aqueous suspension of starch is the main point in determining the best processing conditions and better quality control of the final products.²

Poly(vinyl alcohol) (PVA) is a hydrophilic polymer that can be added in a small amount into a suspension to increase its viscosity, so that settlement of particles during storage and transportation is substantially prevented.^{3,4} Starch/PVA blend has recently attracted much attention as a biodegradable blend that

significantly improves the material properties when compared to the pristine polymer.^{5–8}

Rheological study of aqueous suspension of Starch/PVA is an important step in the characterization of its functional properties. Due to numerous uses of starch suspension, many attempts have been made to identify its rheological characteristics. Acosta-Osorio *et al.*⁹ analyzed the apparent viscosity of starch in different starch/water suspensions using a rapid viscosity analyzer system. A mathematical model was used for the interpretation of the apparent viscosity of starch aqueous suspensions during agitation. Che *et al.*¹⁰ investigated the effect of starch content on the rheological properties of dilute aqueous solution of cassava starch (starch concentration below 1 wt %). A similar study was done by Keshani *et al.*¹¹ in which the rheological properties of pomelo juice concentrates were studied. Zhang

This article was published online on 7 July 2016. An error was subsequently identified in the reference section. This notice is included in the online and print versions to indicate that both have been corrected 20 July 2016.

© 2016 Wiley Periodicals, Inc.

*et al.*¹² carried out the rheological study on aqueous solutions of a new polysaccharide-based polyampholyte under different operational conditions. The results showed the Power law model could describe the rheological behavior of aqueous solutions of polysaccharide well. Raina *et al.*¹³ prepared chemically modified rice starch solutions. They showed that the effect of modification on the rheological properties is similar for all three kinds of starches used in solutions. Herrmann *et al.*¹⁴ developed a rheological prediction model for food suspensions and emulsions. They used artificial networks to predict the rheological parameters of the Herschel–Bulkley model. The effect of damaged starch on the rheological properties of heated and unheated wheat starch suspensions was investigated by Barrera *et al.*¹⁵

Metal oxides are usually used as additives in polymer-based composites. TiO₂ nanoparticles are produced in large scale. Also, TiO₂ is commonly considered as a sound material for humans.¹⁶ Many attempts have been made to investigate the effect of TiO₂ nanoparticles on the starch-based materials.^{17–21} Hejri *et al.*¹⁸ studied the parameters that affected the mechanical properties of starch/PVA/TiO₂ nanoparticle film using the full factorial experimental design approach. They also considered thermal properties of the resulting films. Fei *et al.*²⁰ assessed the properties and structure of starch/poly(ϵ -caprolactone) composites due to the addition of TiO₂ nanoparticles. Yun *et al.*¹⁹ synthesized starch/PVA/TiO₂ nanocomposite films. They evaluated the physical properties of the prepared nanocomposite films, such as tensile strength, elongation at fracture, degree of swelling, solubility, and water vapor absorption. Structural changes correlated with interactions between starch, TiO₂, and ZnSe were analyzed by Bernazzani *et al.*¹⁷ Yuthavisuthi *et al.*²¹ performed the modification of mechanical properties of biodegradable materials associated with TiO₂ nanoparticles.

In spite of many studies carried out to identify the effect of TiO₂ nanoparticles on the physical, mechanical, and thermal properties of starch/PVA/TiO₂ nanocomposite films,^{17–21} there is a lack of information about the rheological behavior of starch/PVA/TiO₂ nanofluids.

The current study investigates the rheological behavior of starch/PVA/TiO₂ nanofluids. Hydrodynamic interactions, Brownian forces among nanoparticles, attractive van der Waals forces, and repulsive electrostatic forces effect on the rheology and flow of nanofluid suspensions. In some studies, it is reported that the addition of nanoparticles, and the increase in the shear rate, decreases the viscosity of some non-Newtonian nanofluids.^{22–24} The creation of complex structures and competition between starch and PVA on the surface of nanoparticle will cause a change in rheological parameters of nanofluid suspensions. So the interplay between starch, PVA, and TiO₂ nanoparticle concentrations in aqueous media is an important key to approach. The current study is directed to investigate this idea for the starch/PVA/TiO₂ nanofluids. For this purpose, the obtained rheological data for starch/PVA suspensions are fit on linear, Power law, and Bingham models. Then, the best-fit model for starch/PVA suspensions is applied for starch/PVA/TiO₂ nanofluids. An analysis of variance (ANOVA) was carried out to assess the main and interactive effects of adding PVA and TiO₂

on the rheological parameters of the selected model for suspension systems. However, some investigations were carried out on the rheological behavior of aqueous starch suspensions.^{2,9–11,13–15} There is no statistical analysis of the parameters that influenced the rheological behavior of starch/PVA/TiO₂ nanoparticles suspension. Furthermore, there are no publications about the effect of the addition of TiO₂ nanoparticles on the rheological behavior of starch/PVA blend suspensions.

EXPERIMENTAL

Materials

Extra pure grade of corn starch obtained from Kianchem Co. (Iran). PVA (Merck, Germany) with a molecular weight of 70,000 g/gmol, was used as a suspending agent. TiO₂ nanoparticles with an average diameter of 10 nm (Nanostructured and Amorphous Materials, Inc. USA) were employed. Double distilled water was used to prepare aqueous suspensions.

Preparation of Starch/PVA Suspensions

The viscous, soft suspension was created by cooking corn starch in water at a temperature above its gelatinization point. The appropriate amount of starch was added to distilled water during gentle agitation at 30 °C for 15 minutes. The slurry was heated in a hot water bath while stirring at 150 rpm and 85 °C. A specific amount of PVA was added to the slurry while stirring. After placing the slurry in hot water bath for 30 minutes, it was cooled rapidly in another water bath at ambient temperature while stirring at 150 rpm for 15 minutes.

Preparation of Starch/PVA/TiO₂ Nanofluids

A definite amount of TiO₂ nanoparticles was added to water, and the suspension was subjected to ultrasonic vibration for 30 minutes to disperse TiO₂ nanoparticles. An appropriate amount of starch was added to mixture while stirring at 150 rpm for 15 minutes at room temperature. The suspension was placed in a hot water bath for 10 minutes, and then was stirred by a mechanical mixer with 150 rpm at 85°C for about 30 minutes before PVA was added to the suspension. After placing the slurry in a hot bath for 30 minutes, it was cooled rapidly in another water bath to ambient temperature while being stirred at 150 rpm for 15 minutes. Since the band gap energy of TiO₂ nanoparticles for photocatalytic reaction is about 3.2 eV, which corresponds to photons with a wavelength of about 388 nm (UV light), the suspensions were held in dark glass bottles to protect from illumination of light.¹⁶

Rheological Measurements and Analysis

Rheological characteristics of suspensions were measured using a DVIII-Ultra Brookfield rheometer. The SC4-18 spindle was selected for the measurement range between 10 and 100% torque scale. The rheometer tests were carried out using 8 mL of each sample. The shear–stress was measured on a shear rate range of 52–290 s⁻¹. In order to control the temperature, the rheometer was connected to a constant temperature bath (Wiscircu WCL-P8/Korea), which was able to maintain temperature uniformity within ± 0.1 °C. The resulting stress and shear rate data of starch suspensions were analyzed using the Newton, Bingham, and Power-law models. The best model for determining the rheological behavior of suspensions was selected using

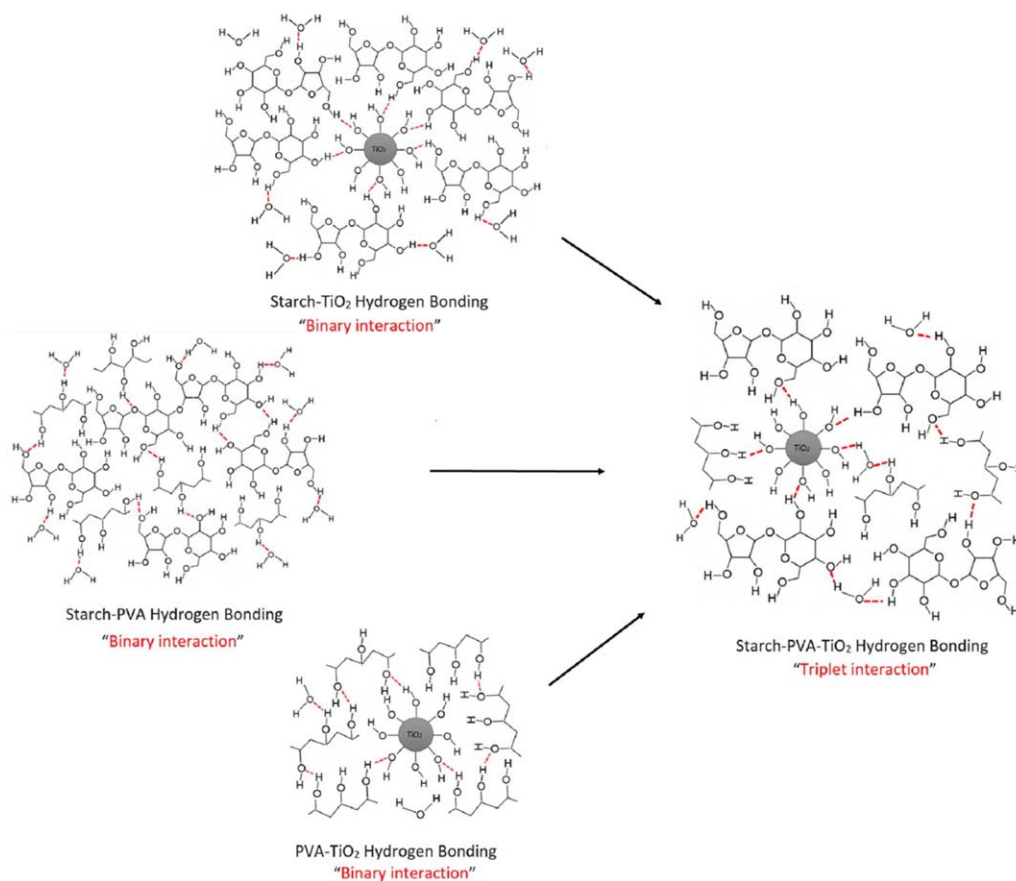


Figure 1. The possible kinds of hydrogen bonds formed in the starch-PVA-TiO₂ suspensions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the coefficient of determination (R^2) of data fitting. The rheometrical parameter changes of the selected model, due to the addition of PVA and TiO₂ nanoparticles, were considered through the experimental design technique.

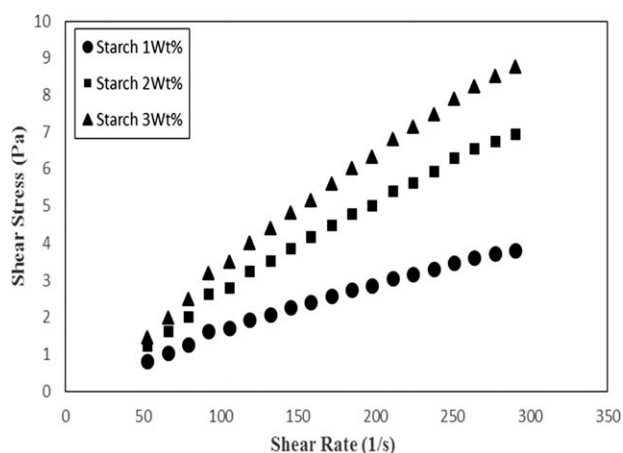


Figure 2. The shear stress as a function of the shear rate for starch suspensions as base fluid.

RESULTS AND DISCUSSION

The electrostatic attractions among hydrogen and oxygen atoms in the starch-PVA-TiO₂ suspensions happened due to electron deficiency of hydrogen and high electronegativity of oxygen. These intermolecular interactions between hydrogen and oxygen atoms are called hydrogen bonds. Figure 1 presents a schematic illustration of the possible kinds of hydrogen bonds in the starch-PVA-TiO₂ suspensions. Intermolecular hydrogen bond interactions between the molecules (the starch, PVA, and TiO₂ nanoparticles) in suspension can affect the rheological behavior. In the following section, this effect was considered by rheological measurements. The experimental data from the rheometry tests of dilute starch suspensions at 1, 2, and 3 wt % starch [Figure 2(a)] were fit to the Newton, Bingham, and Power law models for the evaluation of rheometrical parameters of the models (Table I).

According to the R^2 values in Table I, the Power law model is an appropriate rheological model for the starch dilute suspensions in the range of 1–3 wt % starch. The parameters K and n in the Power law model are the consistency index and the flow behavior index, respectively. The magnitude of the flow behavior index represents the rheological behavior of the fluid. When it is less than one unit, the fluid is shear-thinning behavior, and

Table I. The Rheometrical Parameters of the Newton, Bingham, and Power Law Models

Starch (wt %)	Model							
	Newton $\tau = \mu \dot{\gamma}$		Bingham $\tau = \tau_0 + \mu \dot{\gamma}$			Power law $\tau = K \dot{\gamma}^n$		
	μ	R^2	τ_0	μ	R^2	K	n	R^2
1	0.0143	0.9637	0.3702	0.0124	0.989	0.0278	0.8766	0.9899
2	0.0252	0.9899	0.2669	0.0239	0.9935	0.0279	0.9833	0.9951
3	0.0317	0.9926	0.2195	0.0306	0.9941	0.0297	1.0037	0.9966

when it is more than one unit, the fluid has shear-thickening behavior. In these conditions, $K\dot{\gamma}^{n-1}$ is equal to the apparent viscosity of the fluid. In the special condition that the flow behavior index is equal to one, the suspension is Newtonian and K is the viscosity.²⁵

A hydrophilic polymer such as PVA may be used to reduce the settlement of particles in aqueous suspensions during transportation and storage.^{3,4} It was observed that the presence of PVA in starch suspensions will affect rheological behavior of suspensions. To illustrate the rheological characteristics of starch/PVA suspensions shown in Figure 3, the logarithm of the shear stress was plotted against the logarithm of the shear rate for the suspensions with three different starch concentrations and four different PVA concentrations.

The R^2 values ($R^2 \approx 1$) for the straight lines in a log–log plot accurately illustrate the behavior of experimental data. The Power law model parameters K and n are plotted versus PVA in Figure

4. The flow behavior index (n) of suspensions with 1 and 2 wt % starch concentrations increases with an increase in PVA concentration, while the flow behavior index (n) of the suspension with 3 wt % starch has no regular variation. The consistency coefficient (K) of the suspension with 3 wt % starch concentration is affected by the PVA concentration, while an increase in PVA concentration has no significant effects on the consistency coefficient (K) of suspension with 1 and 2 wt % starch concentration. It reveals that there is an interactive effect between the starch and PVA at high starch concentration in the suspensions.

The design of experiment was carried out using two-level factorial design with four center point and three replicates to assess the main and interactive effects of adding PVA and TiO₂ on the rheological parameters of the Power Law model for starch suspensions. It should be noted that an interaction occurs when the effect of changing one factor (the starch, PVA, or TiO₂ concentration) depends on the level of other factors. In general, all level

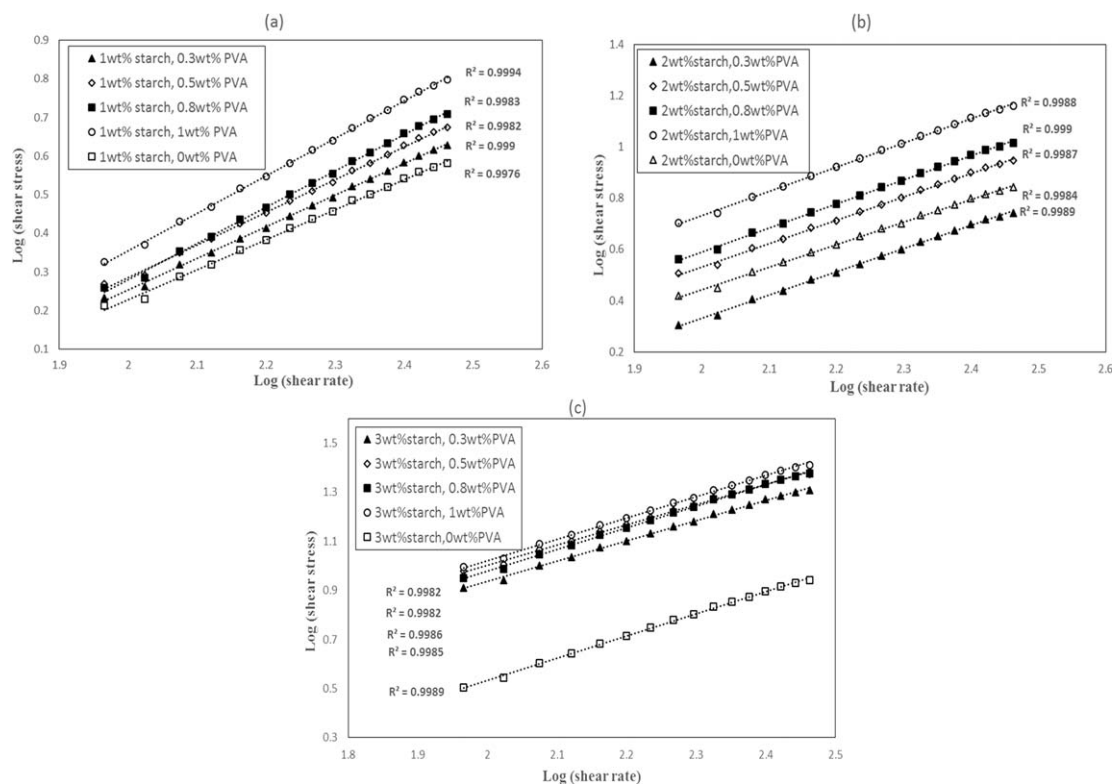


Figure 3. The logarithm of the shear stress as a function of the logarithm of the shear rate for starch/PVA suspensions: (a) 1 wt % starch, (b) 2 wt % starch, and (c) 3 wt % starch.

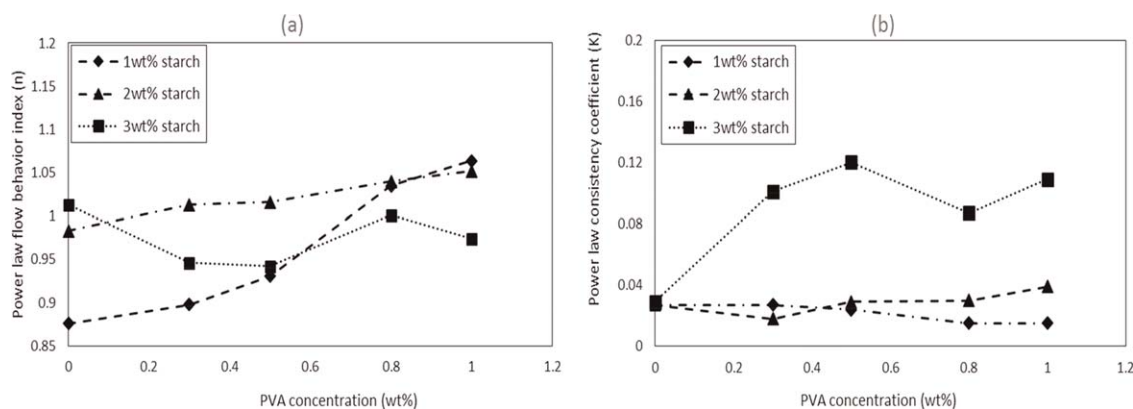


Figure 4. The effects of starch and PVA concentrations on the Power law model parameters: (a) flow behavior index and (b) consistency coefficient.

Table II. ANOVA for Flow Behavior Index (n)

Source	Effect	Sum of squares	df	Mean square	F value	p value	% contribution
(A) Starch concentration	0.017	0.0006	1	0.0006	1.7167	0.2315	1.73
(B) PVA concentration	0.07	0.0097	1	0.0097	28.6694	0.0011	29.00
AB	-0.11	0.0229	1	0.0229	67.7127	<0.0001	68.49
Residual	—	0.0024	7	0.0003	—	—	—
Pure Error	—	0.0003	6	0.0000	—	—	0.78

combinations of the starch, PVA, and TiO_2 concentrations are studied using the experimental design. The resulting data are statistically treated using ANOVA. ANOVA is a powerful method that surveys the main and interactive effects on the experimental data. The procedure used to calculate the parameters in the ANOVA has been explained in the experimental design textbooks.^{26,27} The ANOVA for the flow behavior index is shown in Table II. According to the selected confidence level of 95%, the main and the interactive effects of each factor with p values of <0.05 are considered as significant effects. The effect of each factor quantifies its importance.

The effect of PVA concentration on the flow behavior index is larger than that of starch concentration. The interactive effect between starch and PVA concentrations (AB) is relatively larger than the other factors and has a significant effect on the flow behavior index (n). This means that the effect of the starch concentration depends on the presence of PVA and vice versa. This is due to the fact that association of hydroxyl groups ($-\text{OH}$) of PVA in aqueous suspension of starch tend to form strong

hydrogen bonding with starch that has significant influence on the rheological behavior of suspension.^{28–31} The ANOVA for the consistency coefficient is illustrated in Table III. All factors and interactions have positive and significant effect on the consistency coefficient (K). Starch concentration has the largest effect among the selected factors and interactions.

In definition, an interaction is the influence of changing one factor on responses that depend on the level of other factors. In this case, alteration of flow behavior index with change in starch concentration depends on the presence of PVA. In the presence of PVA, the flow behavior index decreases by an increase in starch concentration from 1 to 3 wt %. A similar trend observed by variation of PVA concentration from 0 to 1 wt % when starch concentration is 1 and 3 wt %. This may be attributed to strong hydrogen bonding between the molecules of PVA and starch. In the absence of PVA, the flow behavior index increases by increasing the starch content. The effect of the strong hydrogen bond among PVA and starch on the

Table III. ANOVA of Consistency Coefficient (K)

Source	Effect	Sum of squares	df	Mean square	F value	p value	% contribution
(A) Starch concentration	0.068	0.0093	1	0.0093	59.0246	0.0001	42.78
(B) PVA concentration	0.048	0.0046	1	0.0046	29.1189	0.0010	21.11
AB	0.063	0.0078	1	0.0078	49.5872	0.0002	35.94
Residual	—	0.0011	7	0.0002	—	—	—
Pure error	—	0.0000	6	0.0000	—	—	0.16

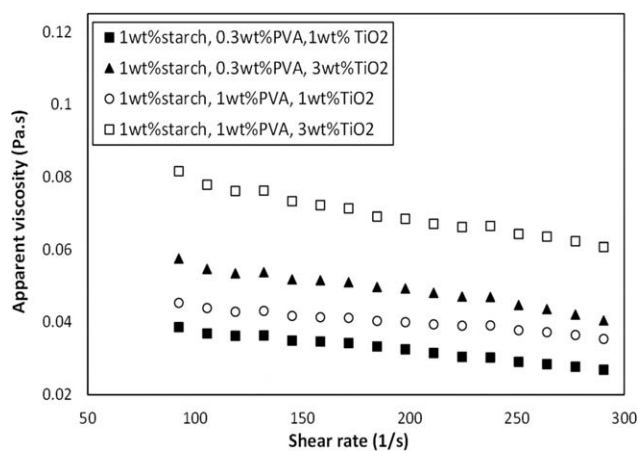


Figure 5. The apparent viscosity of 1 wt % starch/PVA/TiO₂ nanofluids as a function of shear rate at 30 °C.

physical, thermal, and mechanical properties of the starch/PVA blend has been mentioned by many authors.^{28,29,32,33} The results show that the starch concentration has a greater effect on the consistency coefficient than the PVA concentration. When there is no PVA in suspension, the consistency coefficient (K) does not significantly change due to the change in starch concentration from 1 to 3 wt %. However, the consistency coefficient (K) is noticeably increased in the presence of PVA. This behavior also could be related to the interactions among the starch and PVA molecules. Hydrogen bonding between starch and PVA also causes an increase in the consistency coefficient (K) when starch concentration is 3 wt %.

The effect of interactions between starch and PVA concentration (AB) has a negative effect on the flow behavior index (n) and a positive effect on consistency coefficient (K). This means that the AB interactions decreases the flow behavior index (n) and increases the consistency coefficient (K) as starch concentration increases.

In the following section, the effect of adding TiO₂ nanoparticles on the Power law model parameters is considered. The apparent viscosity, as a function of the shear rate at 30 °C, for nanofluids containing 1 wt % starch concentration and different amounts of PVA and TiO₂ concentrations are presented in Figure 5. The apparent viscosity decreases as the shear rate increases. The

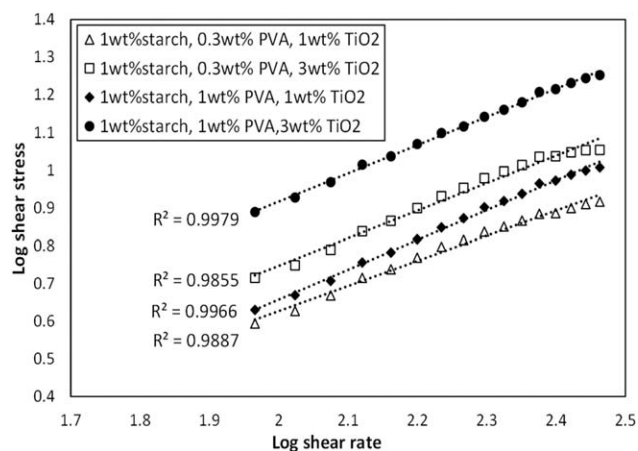


Figure 7. Logarithm the shear stress as a function of the logarithm of the shear rate for starch/PVA/TiO₂ suspensions.

shear-thinning behavior was depicted for all nanofluids with 1 wt % starch concentration.

Adding TiO₂ nanoparticles in the suspensions with 3 wt % starch concentration changes their rheological behavior. Figure 6(a) presents the apparent viscosity of the nanofluids, containing 3 wt % starch and 0.3 wt % PVA with two different nanoparticle concentrations, as a function of the shear rate. This figure shows that the nanofluid containing 1 wt % TiO₂ exhibited shear-thinning behavior. Similar behavior was observed for the suspension without nanoparticles. It is illustrated in Figure 6(a) that the shear-thinning behavior of nanofluids is changed with an increase in the nanoparticle concentration from 1 to 3 wt %. As shown in Figure 6(b), the nanofluids containing 3 wt % starch and 1 wt % PVA with two different nanoparticle concentrations show shear-thickening behavior. The suspension without nanoparticle exhibits different rheological behaviors. These different trends are due to the presence of binary and triplet interactions between starch, PVA, and TiO₂ nanoparticles.

Figure 7 presents the log–log plot for starch concentration of 1 wt %, and several PVA and TiO₂ concentrations. Other prepared suspensions exhibited similar behavior. The coefficients of determination (R^2) for all responses were >0.98 .

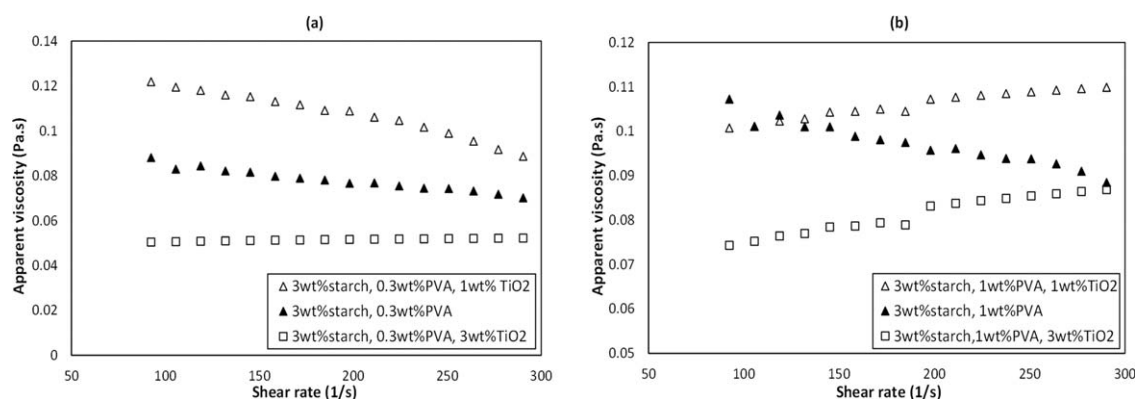


Figure 6. The apparent viscosity as a function of the shear rate for starch/PVA/TiO₂ nanofluids: (a) 0.3 wt % PVA and (b) 1 wt % PVA.

Table IV. ANOVA for Flow Behavior Index (n)

Source	Effect	Sum of squares	df	Mean square	F value	p value	% contribution
(A) Starch concentration	0.3	0.53	1	0.53	1884.04	<0.0001	76.27
(B) PVA concentration	0.12	0.081	1	0.081	288.47	<0.0001	11.68
(C)TiO ₂ concentration	0.062	0.023	1	0.023	82.75	<0.0001	3.35
AB	0.032	0.00611	1	0.00611	21.83	0.0002	0.88
AC	0.051	0.015	1	0.015	55.22	<0.0001	2.24
BC	0.042	0.01	1	0.01	36.91	<0.0001	1.49
ABC	0.022	0.00284	1	0.00284	10.15	0.0049	0.41
Curvature	0.002	0.02	1	0.02	71.78	<0.0001	2.91
Pure error	—	0.0053	19	0.00028	—	—	0.77

The results were scrutinized and, besides the main effects of the interactions of factors on each other, were investigated by evaluating the ANOVA. The ANOVA for the flow behavior index (n) as a response is shown in Table IV.

Factors with p values of <0.05 affect the response significantly. Based on p value, starch concentration (A), PVA concentration (B) and TiO₂ nanoparticle concentration (C), and binary and triplet interactions AB, AC, BC, and ABC have significant effects on the flow behavior index (n). Figure 8(a) shows the effect of starch, PVA, and TiO₂ nanoparticle concentrations on the flow behavior index (n). In each level combination of PVA and TiO₂ nanoparticle concentrations, the flow behavior index (n) increases by the increase in starch concentration from 1 to 3 wt %. Related to the crisscross lines in Figure 8(a), the interactions between PVA and TiO₂ at 1 wt % of PVA concentration are observed. As shown in Figure 4(a), at a PVA concentration of 1 wt %, the flow behavior index decreases by an increase in starch concentration. In Figure 8(a), it is shown that adding TiO₂ nanoparticles reverses the behavior under the same conditions. It also illustrates that the flow behavior index increases by increasing the PVA concentration from 0.3 to 1 wt % in all level combination of starch concentrations and TiO₂ nanoparticle concentrations. As shown in Figure 4(a), the flow behavior index of suspensions with a starch concentration of 3 wt % decreases

by an increase in PVA concentration from 0 to 1 wt %. This can be attributed to the strong interactions among the molecules of PVA and starch. Hydrogen bonding is affected by the incorporation of TiO₂ nanoparticles in suspensions. There is a strong hydrogen bond interaction between PVA and TiO₂, which is in agreement with the results of some other studies.³⁴ The presence of hydroxyl groups (—OH) in PVA polymer tend to cause strong hydrogen bonding with starch and TiO₂.^{28–30} By variation of PVA concentration from 0.3 to 1 wt %, the amount of hydroxyl groups (—OH) in suspension increases and, subsequently, the hydrogen bonding among the PVA and starch chains and TiO₂ nanoparticles are increased. Hydrogen bond formation decreases the mobility of the polymer chains and forms the polymeric lattice that affects the rheological characteristics of the nanofluids.²² Furthermore, interactions between starch and TiO₂ nanoparticles lead to structural changes in starch.¹⁷ The structural change in starch in the presence of TiO₂ is in accordance with the results of research done by Bernazzani *et al.*¹⁷ The flow behavior index (n) in the absence of TiO₂ nanoparticles is decreased by increasing PVA concentration, but in the presence of TiO₂ nanoparticles, it increases. Except for suspension containing 1 wt % of starch and 1 wt % of PVA, the flow behavior index of all other nanofluids is increased by increasing the nanoparticles concentration as shown in Figure 8(a). In the case of 1 wt % of starch and 1 wt % of

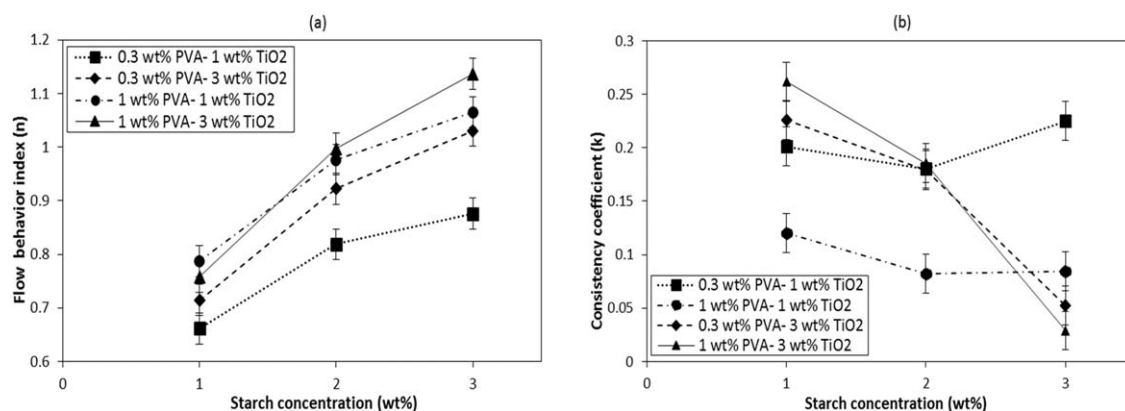
**Figure 8.** Effects of adding TiO₂ on (a) flow behavior index (n) and (b) consistency coefficient (K) of starch/PVA suspensions.

Table V. ANOVA for Consistency Coefficient (K)

Source	Effect	Sum of squares	df	Mean square	F value	p value	% contribution
(A) Starch concentration	-0.1	0.066	1	0.066	257.53	<0.0001	36.71
(B) PVA concentration	-0.052	0.016	1	0.016	64.19	<0.0001	9.15
(C)TiO ₂ concentration	-0.015	0.001432	1	0.001432	5.62	0.0285	0.8
AB	-0.030	0.005315	1	0.005315	20.86	0.0002	2.97
AC	-0.098	0.058	1	0.058	228.28	<0.0001	32.54
BC	0.059	0.021	1	0.021	80.78	<0.0001	11.52
ABC	0.025	0.003648	1	0.003648	14.31	0.0013	2.04
Curvature	-0.00041	0.002772	1	0.002772	10.88	0.0038	1.55
Pure error	—	0.004842	19	0.0002548	—	—	2.71

PVA shown in Figure 8(a), the slight decrease in flow behavior index occurs in the presence of TiO₂ nanoparticles because of high relative ratio of PVA to starch. Different amounts of hydroxyl groups (—OH) in nanofluids, with respect to different amounts of PVA and starch, lead to various hydrogen bonding among PVA and TiO₂ nanoparticles. It causes the different rheological behavior of nanofluids. Referring to the contribution of the starch–TiO₂ (AC) and starch–PVA (AB) interactions in Table IV, it should be mentioned that, at 1 wt % of starch concentration, the probability of formation of hydrogen bonding among the starch and TiO₂ nanoparticles is more than that of among the starch and PVA.

ANOVA for the consistency coefficient (K) is shown in Table V. According to the p value, all factors and interactions significantly effect on the consistency coefficient (K).

The effect of starch concentration on the consistency coefficient of nanofluids is shown in Figure 8(b). It is observed that the consistency coefficient of nanofluids containing 3 wt % of TiO₂ nanoparticles decreases by an increase in starch concentration. However, it passed a minimum for nanofluids containing 1 wt % of TiO₂ nanoparticles. The minimum point could be related to the starch–PVA–TiO₂ interactions (ABC). The diminishing trend in Figure 8(b) is in contrast to what is observed in Figure 4(b) in the absence of TiO₂ nanoparticles. This is due to the presence of TiO₂ nanoparticles in suspension which causes major interactions with starch and PVA. It could be attributed to strong bonding between starch and TiO₂ nanoparticles. The contribution of the starch–TiO₂ interactions (AC) is more than other interactions. Figure 8(b) shows that the consistency coefficient decreases by the increase in the TiO₂ nanoparticle concentration at the starch concentration of 3 wt %. This is related to interactions between starch and TiO₂ nanoparticles, which consequently affect the interactions between starch and PVA. The trend is transverse at the same conditions, but at a starch concentration of 1 wt %. According to Table III, starch concentration has a larger effect on the consistency coefficient (K) than the PVA concentration. When starch concentration is at 1 wt %, the effect of PVA concentration is more than that of 3 wt %. On the other hand, the strong interactions between PVA and TiO₂ nanoparticles concentrations have more influence at 1 wt % of starch concentration than 3 wt %. These trends justify the

existence of a minimum in the consistency coefficient (K) in the presence of TiO₂ nanoparticles.

The rheological behavior of nanofluids was changed as the concentration of TiO₂ nanoparticles was increased. These different behaviors were ascribed to the presence of binary and triplet interactions between starch, PVA, and TiO₂ nanoparticles. According to the ANOVA, the interactions have significant effects on the rheological characteristics of nanofluids.

CONCLUSIONS

The effects of starch concentration, PVA concentration, and the presence of TiO₂ nanoparticles on the consistency coefficient (K) and flow behavior index (n) of the Power law model were investigated using ANOVA. Results demonstrate the major effects of the presence of PVA and TiO₂ nanoparticles in starch suspension on the rheological characteristics. The consistency coefficient (K) and the flow behavior index (n) are influenced by the amount of PVA and TiO₂ and indicate strong hydrogen bonding between molecules. Variation of bonding intensity between starch, PVA, and TiO₂ nanoparticles leads to change in the rheological behavior of nanofluids. Comparison between trends of The Power law model parameters shows an incorporation of TiO₂ nanoparticles causing intermolecular hydrogen bonding combination of TiO₂, PVA, and starch and resulting in interactions between starch–PVA, starch–TiO₂, and PVA–TiO₂. Consequently, different rheological behaviors of starch/PVA/TiO₂ nanofluids comprising starch/PVA blend suspensions are observed.

NOMENCLATURE

A	starch concentration
AB	binary interactions between A and B
ABC	triple interactions between A, B, and C
AC	binary interactions between A and C
ANOVA	analysis of variance
B	PVA concentration
BC	binary interactions between B and C
C	TiO ₂ concentration
df	degree of freedom
K	consistency index

n	flow behavior index
PVA	poly(vinyl alcohol)
p value	probability value
TiO ₂	titanium dioxide

ACKNOWLEDGMENTS

The authors specially thank Brian C. Yohe for his kindness.

REFERENCES

1. BeMiller, J.; Whistler, R. *Starch: Chemistry and Technology*; Elsevier: OXFORD, **2009**.
2. Xie, F.; Halley, P. J.; Avérous, L. *Prog. Polym. Sci.* **2012**, *37*, 595.
3. Cruse, J. W.; O'Callaghan, W. Google Patents (**1989**).
4. Takada, S. Google Patents (**1998**).
5. Sreekumar, P. A.; Al-Harhi, M. A.; De, S. K. *Polym. Eng. Sci.* **2012**, *52*, 2167.
6. Azahari, N.; Othman, N.; Ismail, H. *J. Phys. Sci.* **2011**, *22*, 15.
7. Park, H. R.; Chough, S. H.; Yun, Y. H.; Yoon, S. D. *J. Polym. Environ.* **2005**, *13*, 375.
8. Moeinzadeh, S.; Barati, D.; He, X.; Jabbari, E. *Biomacromolecules* **2012**, *13*, 2073.
9. Acosta-Osorio, A. A.; Herrera-Ruiz, G.; Pineda-Gómez, P.; Cornejo-Villegas, A.; Martínez-Bustos, F.; Gaytán, M. *Mech. Eng. Res.* **2011**, *1*, 110.
10. Che, L.; Li, D.; Wang, L.; Özkan, N.; Chen, X. D.; Mao, Z. *Carbohydr. Polym.* **2008**, *74*, 385.
11. Keshani, S.; Chuah, A. L.; Russly, A. *Int. Food Res. J.* **2012**, *19*, 553.
12. Zhang, L.; Zhou, J.; Hui, P. *Colloids Surf. A* **2005**, *259*, 189.
13. Raina, C.; Singh, S.; Bawa, A.; Saxena, D. *J. Food Process Eng.* **2006**, *29*, 134.
14. Herrmann, J.; Brito Alayón, A.; Trembley, J.; Grupa, U. *J. Food Eng.* **2013**, *115*, 481.
15. Barrera, G. N.; Bustos, M. C.; Iturriaga, L.; Flores, S. K.; León, A. E.; Ribotta, P. D. *J. Food Eng.* **2013**, *116*, 233.
16. Shakouri, A.; Heris, S. Z.; Etemad, S. G.; Mousavi, S. M. *J. Mol. Liquids* **2016**, *216*, 275.
17. Bernazzani, P.; Pandi, H. K. R.; Peyyavula, V. K. *Chem. Biochem. Mol. Biol.* **2009**, *2*, 1.
18. Hejri, Z.; Ahmadvpour, A.; Seifkordi, A.; Zabarjad, S. M. *Int. J. NanoScience Nanotechnol.* **2013**, *8*, 215.
19. Yun, Y. H.; Youn, Y. N.; Yoon, S. D.; Lee, J. U. *J. Ceram. Process. Res.* **2012**, *13*, 59.
20. Fei, P.; Shi, Y.; Zhou, M.; Cai, J.; Tang, S.; Xiong, H. *J. Appl. Polym. Sci.* **2013**, *130*, 4129.
21. Yuthavisuthi, P.; Jarupan, L.; Pechyen, C. *Trans. Nonferr. Metals Soc. China* **2012**, *22*, 697.
22. Shakouri, A.; Ahmari, H.; Hojjat, M.; Zeinali Heris, S. J. *Vinyl Addit. Technol.* **2015**. DOI 10.1002/vnl.21502.
23. Hojjat, M.; Etemad, S. G.; Bagheri, R.; Thibault, J. *Int. Commun. Heat Mass Transfer* **2011**, *38*, 144.
24. Koos, E.; Willenbacher, N. *Science* **2011**, *331*, 897.
25. Irgens, F. *Rheology and Non-Newtonian Fluids*; Switzerland: Springer International, **2014**.
26. Montgomery, D. C. *Design and Analysis of Experiments*; John Wiley & Sons, **2008**.
27. Madarshahian, R.; Caicedo, J. M.; Zambrana, D. A. In "Evaluation of a time reversal method with dynamic time warping matching function for human fall detection using structural vibrations." *Model Validation and Uncertainty Quantification*, Volume 3. Springer International Publishing, 2014, pp 171–176. [Correction made here after initial online publication.].
28. Othman, N.; Azahari, N.; Ismail, H. *Malaysian Polym. J.* **2011**, *6*, 147.
29. Follain, N.; Joly, C.; Dole, P.; Bliard, C. *Carbohydr. Polym.* **2005**, *60*, 185.
30. Parvin, F.; Khan, M. A.; Saadat, A.; Khan, M. A. H.; Islam, J. M.; Ahmed, M.; Gafur, M. *J. Polym. Environ.* **2011**, *19*, 1013.
31. Barati, D.; Moeinzadeh, S.; Karaman, O.; Jabbari, E. *Polymer* **2014**, *55*, 3894.
32. Sin, L. T.; Rahman, W.; Rahmat, A.; Khan, M. *Carbohydr. Polym.* **2010**, *79*, 224.
33. Mao, L.; Imam, S.; Gordon, S.; Cinelli, P.; Chiellini, E. *J. Polym. Environ.* **2000**, *8*, 205.
34. Kadem, B. Y. *Int. J. Sci. Technol.* **2011**, *1*, 183.