pH effects on shear thickening behaviors of polystyrene-ethylacrylate colloidal dispersions

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Abstract

In this study, the effects of pH on shear thickening behaviors were investigated based on concentrated dispersions consisting of polystyrene-ethylacrylate (PSt-EA) copolymer nanospheres. The pH values of the above shear thickening fluids were controlled by adding different kinds of acid and alkali solutions, and the rheological testing indicated that the shear thickening behaviors of PSt-EA colloidal dispersions is significantly dependent on the system's pH. Zeta potential of this system tends to be close to zero at a pH of 3 or 9. Since the surface characteristics of copolymer nanospheres were changed, the isoelectric point is 3 in the acid circumstance, while the isoelectric point turns to be 9 by adding alkali. Both decreasing and increasing the pH value near to the isoelectric point can lower the critical shear rate of suspensions and make it easier for the ST behavior to take place. The effect of pH can be qualitatively explained by using a clustering mechanism, which attributes the phenomena to the formation of temporary, hydrodynamic clusters.

Keywords: shear thickening fluid, critical shear rate, pH, zeta potential, PSt-EA

## 1. Introduction

Shear thickening (ST), accompanied by a significant, discontinuous steep increase in viscosity when subjected to an applied stress, is a kind of reversible non-Newtonian behavior existing in concentrated colloidal suspensions [1–6]. Due to their excellent applications in soft armor, damping, and shock absorption, these kinds of shear thickening fluids (STFs) are an attractive

smart material in practice [7, 8]. Most of the previous studies were focused on the influencing factors, applications, and mechanism of STF [9–11]. It was found that the disperse phase includes size, types, shape, monodispersion, volume fraction, and particle interactions, and that the interactions between the disperse phase and the disperse medium were critical for the ST effects [4, 12–16]. Magnetorheological (MR) STF of typical rheological properties has also been reported [17, 18]. Moreover, rheo-optical experiments, neutron scattering, and other technical analysis has demonstrated that the ST behavior was attributed to the formation of temporary, hydrodynamic clusters resulting from lubrication forces and interactions between particles [4, 19–22].

The STFs with high ST effects were favorable for their practical applications in liquid couplings, shock absorbers, and body armors. One of the hot points for improving the STFs is controlling the onset of ST and the maximum change of velocity. It was reported that the surface characteristics exhibited a high influence on the ST behavior; thus the investigation of the detailed mechanism was critical for continuously controlling their rheological properties. The surface charge of the dispersing particles in the STFs greatly affected the stability of the dispersion system via changing the interactions between the dispersing particles. The pH value of the dispersing medium plays a critical role in determining the surface charge of the particles; thus the pH-dependent ST behavior has attracted increasing research interest because it not only supplies a novel way to control the rheological properties of the STFs but is also helpful for understanding the ST mechanism.

ST generally occurs in the deflocculated suspension, which means the overall interparticle force is not attractive [23]. In Stokesian dynamic simulation, interactions between particles are always repulsive hydrodynamic lubrication forces during the ST [24]. Electrostatic stabilization and Brownion motion are two methods which can be adopted to investigate the rheological properties of STF [25, 26]. Results demonstrated that reversible behavior of ST had a close relationship with interparticle force [27]. Because of the repulsive forces, the viscosity of STF in a low shear rate would obviously decrease. ST will disappear when the attractive force is strong enough that a gel is formed [19]. On the other hand, lubrication force is also associated with ST behaviors. The phenomenon of ST existed only when the lubrication force which mainly depended on the surface of the copolymer was strong [28]. Franks *et al* studied the influence of pH on the ST behavior of oxide suspensions [29]. It was concluded that repulsive forces between particles would avoid flocculation in STF so that the homogeneity of suspensions could be ensured. Adjusting the pH of a STF is a useful way to affect the surface charge of particles and further change the repulsive force, which is judged by the magnitude of the zeta potential [30]. The smaller the zeta potential, the smaller the repulsive force will be and the closer pH will get to the isoelectric point. At the isoelectric point of the silica suspensions (pH = 2), the critical shear rate of the system is low. A similar result is observed in alumina suspensions: ST easily takes place near the isoelectric point (pH = 9). However, systematic investigation of pH-dependent ST behavior is still scarce at this point in the research. The study of various kinds of acid and alkali, including organic and inorganic matters and strong and weak substances, was necessary for thoroughly understanding the ST mechanism.

In this work, polystyrene-ethylacrylate (PSt-EA) copolymer nanospheres, which are spherical, monodisperse, and regularly arranged, were prepared by emulsion polymerization. By dispersing these copolymer nanospheres in ethylene glycol, high-performance STF was obtained. To investigate the influence of the pH value on the ST effects, the relative acid or alkali solutions were added into the STF, so that the critical shear rate and the maximum ST
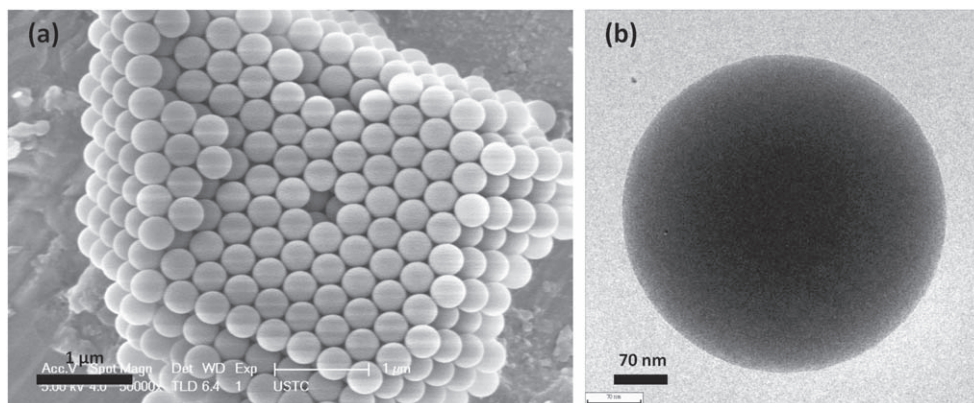
Figure 1. SEM (a) and TEM (b) images of the as-prepared PSt-EA nanospheres.

effect could be selectively controlled. The zeta potential analysis of the STF under different pH conditions indicated that the STF exhibited the optimum ST behavior when the pH was near the isoelectric point of the polymer nanospheres. The influence factors were analyzed and a possible mechanism was proposed.

2. Experimental procedure

2.1. Preparation of PSt-EA nanospheres

All the reagents were of analytical purity and purchased from Sinopharm Chemical Rea Co., Ltd. Styrene was purified with NaOH solutions. Potassium persulfate (KPS) was handled using the recrystallization method. All polymerizations were conducted in a 500 ml three-necked flask. The flask was fixed with a mechanical stirrer, a reflux condenser, and a nitrogen inlet. In a typical synthesis, styrene, acrylate, and ethyl acrylate were first mixed by a mechanical stirrer for 30 min in distilled water. Then KPS was added to the mixture. After 10 min of mixing at room temperature, the flask was heated to 75 °C in a water bath for 6 h. All runs were conducted under a nitrogen atmosphere. The emulsion obtained was centrifuged and then the sediment was redispersed in distilled water. After that, the emulsion was cleaned for 30 min in an ultrasonic cleaner. This procedure was iterated three times. At last, the PSt-EA nanospheres obtained were dried in a vacuum oven at 50 °C.

2.2. Characterization of PSt-EA nanospheres

The microstructure of the nanospheres was investigated by scanning electron microscope (SEM, Sirion 200) and transmission electron microscope (TEM). The SEM and TEM images of PSt-EA nanospheres are shown in figure 1. The microscope view of the synthesized PSt-EA nanospheres indicated that the nanospheres were spherical and monodisperse. At the same time, these copolymer nanospheres were regularly arranged and nonflocculated. By calculating about 50 PSt-EA nanospheres, the average particle size was estimated to be 400 nm.

2.3. Preparation of STFs with different pH values

A certain number of PSt-EA nanospheres were added into ethylene glycol to prepare PSt-EA colloidal dispersions. They were mixed in a ball crusher and rubbed for 24 h in order to obtain a uniform distribution of PSt-EA nanospheres within the suspensions. In order to study the influence of pH, a series of acid and alkali solutions of different concentrations including HCl (0.1 M, 0.2 M, 0.3 M), citric acid (0.5 M, 1.0 M, 2.0 M), sodium citrate (0.1 M, 0.5 M, 1.0 M), sodium acetate (0.1 M, 0.5 M, 1.0 M), NaOH (0.1 M, 0.4 M, 0.7 M), and KOH (0.1 M, 0.4 M, 0.7 M) was prepared. An equal volume of acid or alkali solution was added to the STF to adjust the pH.

2.4. Rheological measurements

The experiments were performed primarily in a stress- and strain-controlled rheometer (Anton-Paar MCR 301) with cone-plate geometry having a cone angle of 0.2° and a diameter of 25 mm. Steady shear tests were conducted on each sample. For steady shear tests, an equilibration time of 180 s was given at the beginning to allow the system to reach steady shear. All the experiments were conducted with a gap size of 0.05 mm at room temperature of 25 °C. In addition, the zeta potential of all samples was measured on ZetaCAD. Because the volume fraction of nanospheres is extremely high, the suspensions should be regarded as strong systems. Limited to the instrument, samples should be diluted by ethylene glycol before measurement.

3. Results and discussion

3.1. Effects of acid on the rheological properties of PSt-EA copolymer dispersions

In order to investigate the effects of acid on PSt-EA copolymer dispersions, acid solutions of different concentrations were added to the STF and then the rheological properties of all samples were investigated. It was found that each sample showed ST behavior and the degree of ST changed by turning the concentration of acid solutions. Firstly, HCl was applied as the controlling reagent. Figure 2(a) shows shear rate–dependent viscosity curves under doping HCl with concentrations varying from 0.1 to 0.2 and 0.3 M. Clearly, with an increase of HCl concentration, the pH decreases. The critical shear rates of the STFs decreased from 622.9 (pH = 5.31) to 416.0 (pH = 4.23) and 356.4 s^{-1}(pH = 3.34), respectively. Thus, the critical shear rate exhibited an increasing tendency with an increase of the pH.

The surface property of the polymer nanospheres was variable under different pH values. Figure 2(b) shows the relationship between zeta potential, critical shear rate, and pH. When the concentration of the added HCl solutions is relatively large, the pH value and zeta potential will both be low. Moreover, critical shear rate decreases under low pH value and zeta potential. That is to say, the addition of HCl solutions is preferred for the starting of the ST behavior. The lower the pH value, the easier the shear thickening. To further study the influence of acid on ST effect, rheological properties of samples with citric acid of different concentrations varying from 0.5 to 1.0 and 2.0 M were also conducted. Similarly, the results of adding citric acid solutions were in accordance with those of adding HCl solutions (figures 3(a) and (b)). As a result, the high acid concentration leads to a lower pH circumstance and the STF exhibits a smaller set shear rate; thus the ST happens more easily.
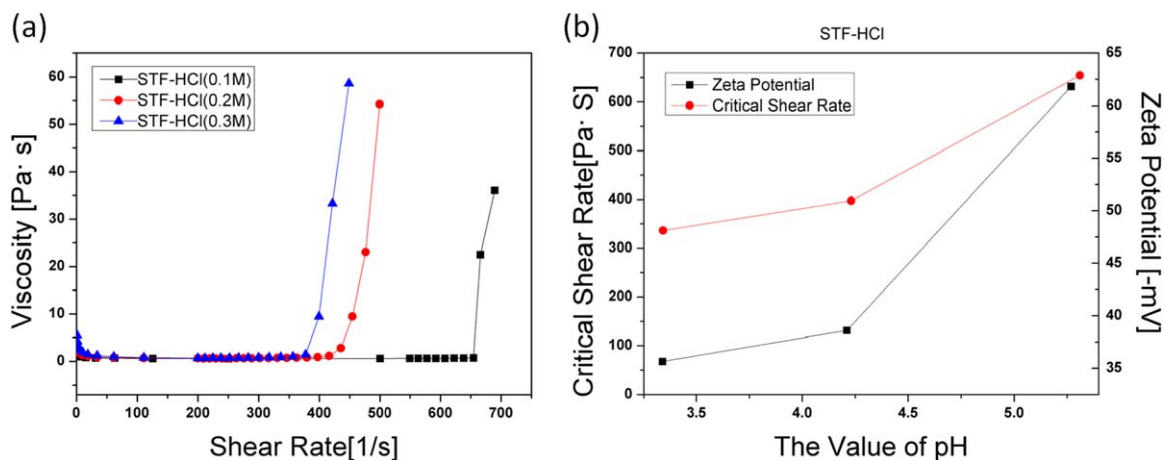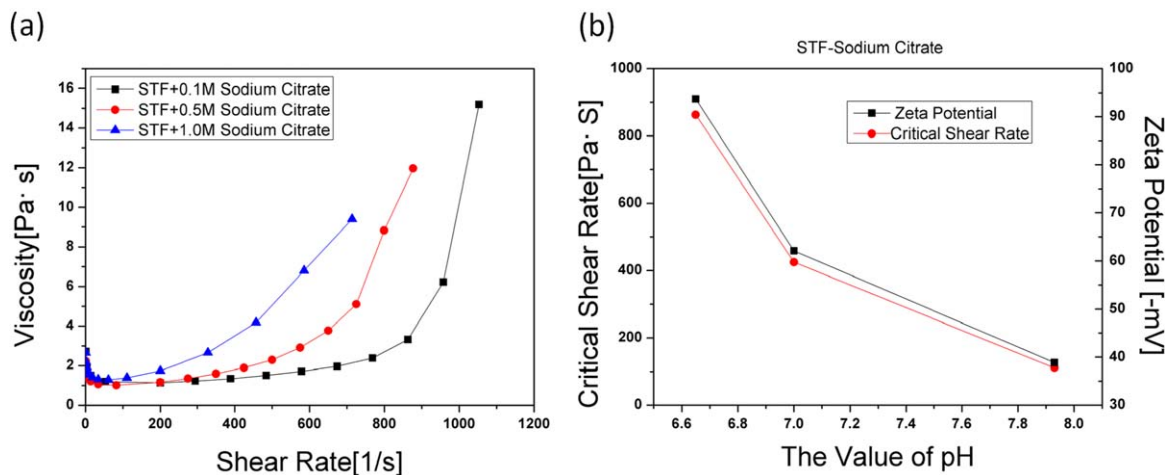
Figure 2. (a) Steady-shear tests; viscosity versus shear rate of PSt-EA suspensions with added HCl of different concentrations (0.1 M, 0.2 M, 0.3 M); (b) Critical shear rate and zeta potential at various pH values.
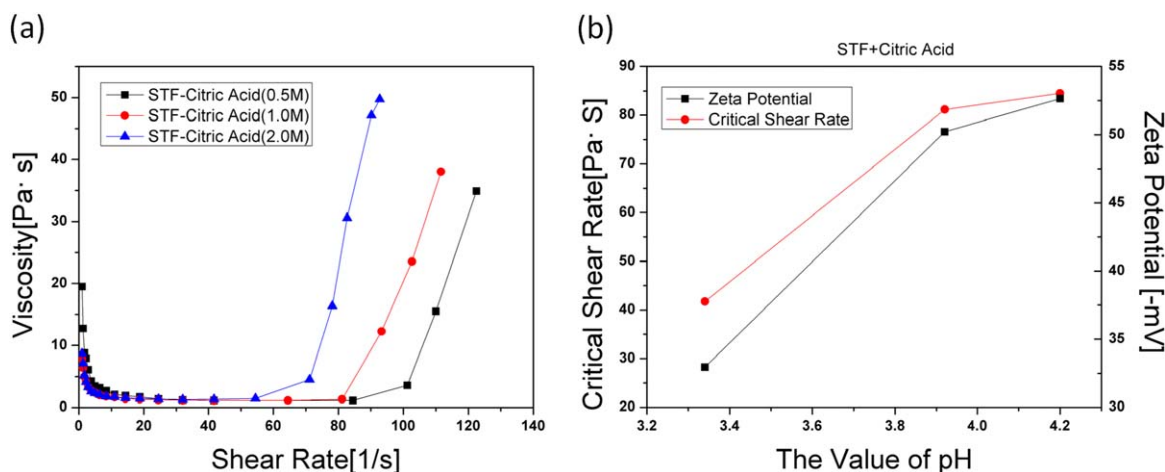
Figure 3. (a) Steady-shear tests; viscosity versus shear rate of PSt-EA suspensions with added citric acid of different concentrations (0.5 M, 1.0 M, 2.0 M); (b) Critical shear rate and zeta potential at various pH values.

The interactions among the polymer nanospheres play a critical role in the ST phenomenon. From the zeta potential curve, it can be concluded that zeta potential becomes smaller with decreasing pH. After adding acid to PSt-EA, the isoelectric point of the system is around 3; thus the repulsive force is relatively small at that pH. A repulsive force between particles was usually caused by electrostatic force, entropy, or spatial interaction. In this work, the STF was prepared by dispersing PSt-EA copolymer nanospheres in ethylene glycol. There were plenty of carboxylate anion groups on the surface of the copolymer nanospheres. The surface of nanospheres was negatively charged, thus repulsive force existed between the dispersed particles. After adding acid solution into suspensions, hydrogen ions reduce the amount of total negative charge and weaken the repulsive force; then the pH value will be close to the isoelectric point (pH = 3). When subjected to shear, the distance between particles will be small and clusters will be easily formed. Therefore, when pH value approaches to the isoelectric

Figure 4. (a) Steady-shear tests; viscosity versus shear rate of PSt-EA suspensions with added sodium citrate of different concentrations (0.1 M, 0.5 M, 1.0 M); (b) Critical shear rate and zeta potential at various pH values.

point, the ST will be very easily achieved by applying a relatively low shear rate [30]. Moreover, the critical shear rate of suspensions will be reduced and the degree of ST strength will be increased. From table 1, it was found that the pH values of STF-HCl (0.3 M) and STF-citric acid (2.0 M) were almost the same, but their zeta potential and critical shear rates have an apparent difference. It can be conjectured that the anions from the added acid will affect the interparticle force in the suspensions and then ST behavior will be influenced.

3.2. Effects of alkali on the rheological properties of the PSt-EA copolymer dispersions

The effects of alkali on PSt-EA copolymer dispersions were concentrated by adding alkali solutions to STF; the rheological properties of all samples were then tested. After adding alkali, the flow properties were weakened and the initial conditions of the system were changed. Figure 4(a) shows the viscosity versus shear rate curves for PSt-EA dispersions with various sodium citrate concentrations varying from 0.1 to 0.5 and 1.0 M. Different from the above acid influence, the zeta potential of the suspensions decreased with the increasing pH after adding an alkali solution. When acid reagent was added, hydrogen ions reduced the negative charges to form –COOH, which caused the appearance of an isoelectric point (pH = 3). Correspondingly, Na$^+$ or K$^+$ reacted with –COO$^-$ to form –COONa or –COOK. In the alkali medium, OH$^-$ changed the surface charges of the nanospheres, which further affected the system's physical properties so the isoelectric point (pH = 9) occurred. From the zeta potential curves, it was found that zeta potential was low at the pH of 9, so the isoelectric point of the system was around 9. When the concentration of added sodium citrate was fairly large, the shear thickening phenomenon presented at a low shear rate. However, with decrement of the added alkali, the pH decreased and moved away from the isoelectric point (pH = 9), and thus the critical shear rate greatly increased (figure 4(a) and table 2). To further investigate the alkali influence, sodium acetate was also introduced to turn the pH value. The result was similar to the sodium citrate case. When the concentration of sodium acetate is large, the pH will be high and the zeta potential will be low. With an increase in the concentration, the pH of suspensions moves close to the isoelectric point and then the critical shear rate apparently is reduced (figure 5).

Table 1. Critical shear rate and zeta potential for the onset of shear thickening of PSt-EA suspensions with acid added.
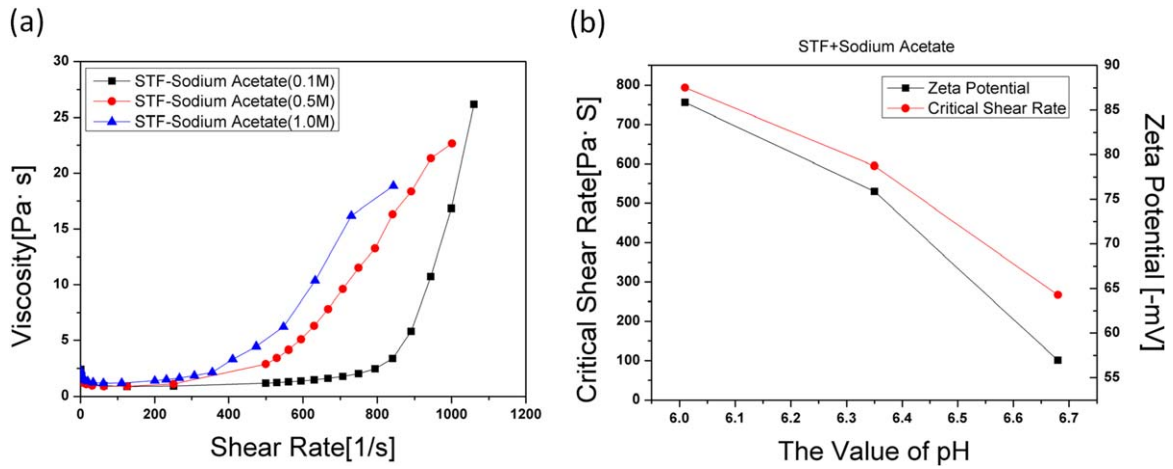
Sample	pH	Critical shear rate ($1\ s^{-1}$)	Zeta potential (mV)	Shown in figure
STF-HCl(0.1 M)	5.31	622.9	−61.83	1
STF-HCl(0.2 M)	4.23	416.0	−38.61	1
STF-HCl(0.3 M)	3.34	356.4	−35.64	1
STF-Citric acid (0.5 M)	4.20	84.5	−52.65	2
STF-Citric acid (1.0 M)	3.92	64.5	−50.22	2
STF-Citric acid (2.0 M)	3.34	41.7	−32.94	2

**Table 2.** Critical shear rate for the onset of shear thickening of PSt-EA suspensions with alkali added.

Sample	pH	Critical shear rate ($1\ s^{-1}$)	Zeta potential (mV)	Shown in figure
STF-Sodium Citrate (0.1 M)	6.65	673.7	−93.69	3
STF-Sodium Citrate (0.5 M)	7.00	200.0	−62.10	3
STF-Sodium Citrate (1.0 M)	7.93	53.2	−38.88	3
STF-Sodium Acetate (0.1 M)	6.01	707.3	−85.86	4
STF-Sodium Acetate (0.5 M)	6.35	561.2	−75.87	4
STF-Sodium Acetate (1.0 M)	6.68	308.0	−56.97	4
STF-NaOH(0.1 M)	7.74	863.2	−96.39	5
STF-NaOH(0.4 M)	8.06	672.0	−56.97	5
STF-NaOH(0.7 M)	8.31	568.4	−43.47	5
STF-KOH(0.1 M)	7.86	857.7	−92.34	6
STF-KOH(0.4 M)	8.15	747.3	−51.57	6
STF-KOH(0.7 M)	8.65	637.7	−45.09	6

    Sodium citrate and sodium acetate are two kinds of salt with strong alkali and weak acid. Here, NaOH and KOH were further chosen as another two additives. After a series of experiments, we found that NaOH of high concentration would destroy the ST effects of PSt-EA copolymer dispersions: the initial viscosity would be extremely high and the flow properties of suspensions would disappear. This is because that pH is nearly at the isoelectric point; suspensions are flocculated by strong attractive forces between particles which makes the viscosity so high that the ST phenomenon cannot be easily tested. To this end, the concentrations of NaOH and KOH were controlled to be 0.1, 0.4, and 0.7 M. Clearly, their
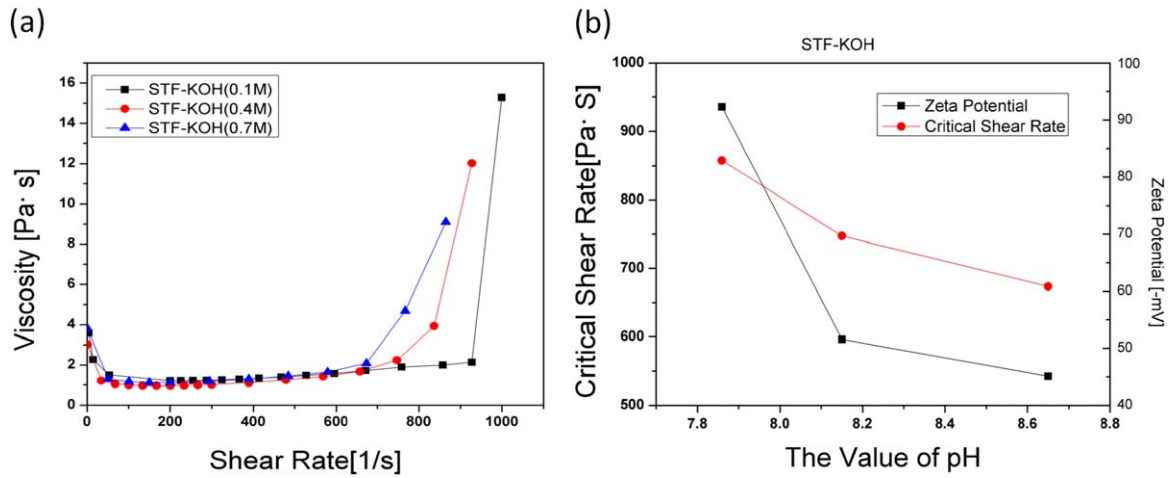
Figure 5. (a) Steady-shear tests; viscosity versus shear rate of PSt-EA suspensions with added sodium acetate of different concentrations (0.1 M, 0.5 M, 1.0 M); (b) Critical shear rate and zeta potential at various pH values.
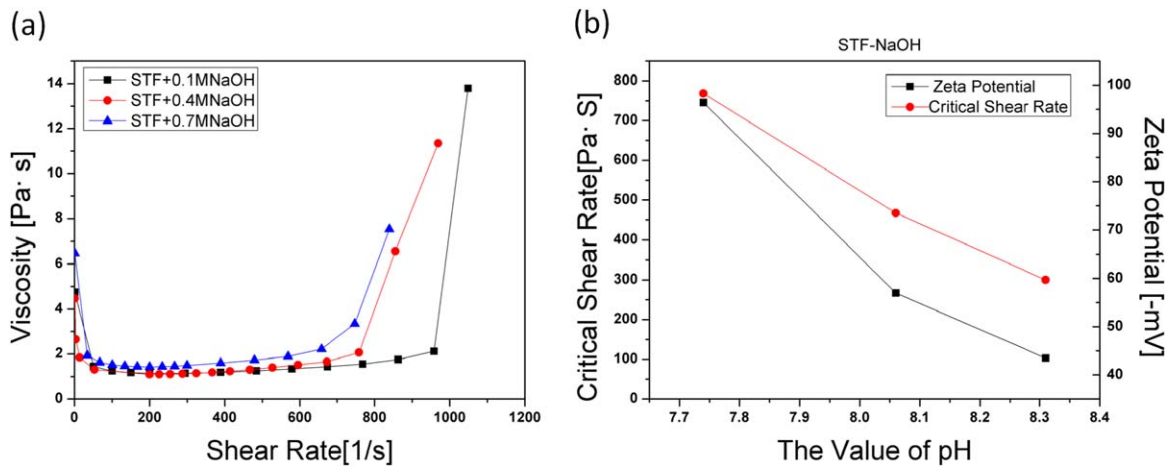

Figure 6. (a) Steady-shear tests; viscosity versus shear rate of PSt-EA suspensions with added NaOH of different concentrations (0.1 M, 0.4 M, 0.7 M); (b) Critical shear rate and zeta potential at various pH values.

influence was nearly the same as that of sodium citrate and with the increasing concentration, the critical shear rate was obviously reduced.

As soon as the alkali solutions were introduced into the PSt-EA–based STFs, their rheological characteristics were changed correspondingly. With an increase in alkali concentration, the zeta potential of suspensions decreased. As pH moved slightly away from the isoelectric point, the critical shear rate was relatively low (figures 6 and 7). In addition, it was noticed that the increasing range of viscosity in the dispersions with alkali was smaller than those with acid. It's inferred that alkali may impact on some functional groups in the surfaces of particles; then the lubrication force and the interactions between particles and disperse phase are both affected, which causes the differences in viscosity.

Figure 7. (a) Steady-shear tests; viscosity versus shear rate of PSt-EA suspensions with added KOH of different concentrations (0.1 M, 0.4 M, 0.7 M); (b) Critical shear rate and zeta potential at various pH values.
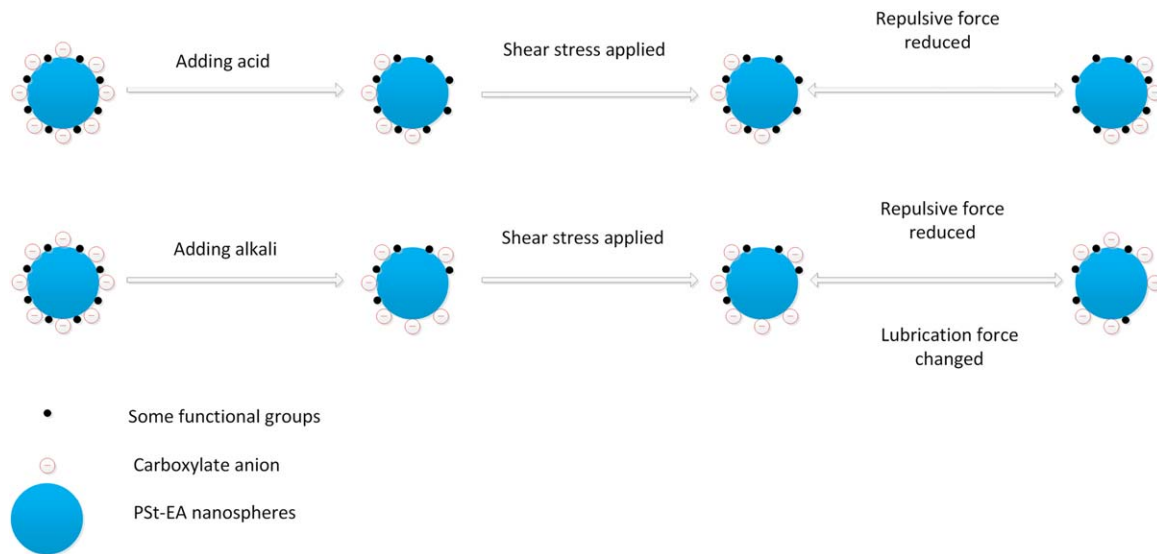
Figure 8. Schematic illustrations of the pH effects.

3.3. The zeta potential of the polymer nanospheres under different pH

Based on the above experimental results, it can be concluded that changing the concentration of added acid or alkali solutions can determine the onset of ST of the PSt-EA copolymer solutions. By using the same kind of acid, the critical shear rate decreases with a decrease in pH. Correspondingly, the results are opposite when the same type of alkali is applied. Figure 8 shows the proposed scheme for the pH effects in our system. First, after separating PSt-EA copolymer nanospheres into ethylene glycol, carboxylate anion groups exist in the surface of dispersed phase nanospheres, making the surfaces of the polymer nanospheres negatively charged. When introducing acid solution into STF, the separation nature of carboxyl groups will be restrained; thus the amount of total negative charge will be reduced because of the decrement
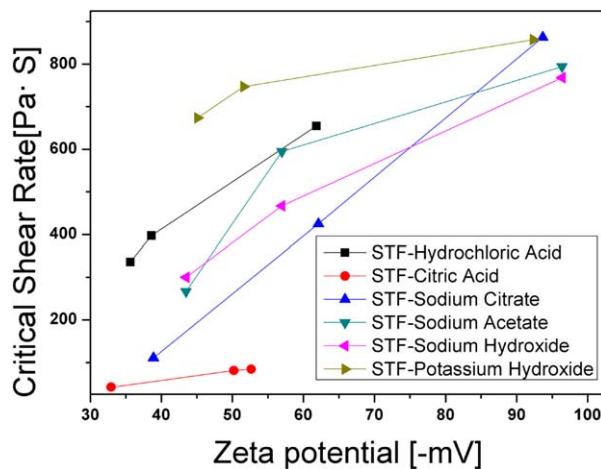
Figure 9. Critical shear rate versus zeta potential of PSt-EA suspensions.

of carboxylate anions, which further weakens the repulsive force. Differently, the alkali solution will greatly change the initial condition of STF. If the alkali concentration is relatively high, the flowing property of suspensions will disappear. It can be inferred that some functional groups in the surfaces of nanospheres are affected by an alkali solution. This change decreases the repulsive force among the polymer nanospheres, which further influences the lubrication force. Finally, the rheological properties of STF will be transformed.

Moreover, the critical shear rates are found to be highly dependent on the zeta potential of samples. Figure 9 shows the relationships between critical shear rate and zeta potential of PSt-EA copolymer dispersions. With the STF and acid/alkali kept the same, the increment of the zeta potential (absolute value) delays the onset of ST. That is to say, the critical shear rate increases with the increasing zeta potential. Zeta potential, which is the characterization of the potential differences between disperse medium and stable fluid layers attached to the discrete phase, is consistent with the stability of colloidal dispersions. When zeta potential (absolute value) increases, the repulsive forces between particles tend to increase. Therefore, the function of dispersing and dissolving are strengthened, which results in resistance to aggregation. To this end, the growth of clusters must be delayed to a high shear rate when zeta potential is large.

4. Conclusions

In this work, the effects of pH on ST behavior of PSt-EA copolymer dispersions were investigated. The as-prepared PSt-EA copolymer nanospheres are spherical, regularly arranged, monodisperse, and nonflocculent. The average diameter is about 370 nm. By dispersing nanospheres in ethylene glycol, suspensions of typical ST behavior were prepared and then a series of samples with different pH were obtained by adding an equal volume of acid or alkali solutions of different concentrations to an equal quality of STF. It can be concluded that pH values have a significant influence on ST behaviors, and that the critical shear rate decreases with the decreasing pH by adding acid; an opposite characteristic is exhibited for the alkali. The influence mechanism was carefully discussed and it was found that the effects of pH on ST behaviors are due to the interactions between particles, especially repulsive forces. Moreover, the critical shear rate increases with the increasing zeta potential (absolute value). If the pH is

away from the isoelectric point, the repulsive forces will be relatively large and the formation of clusters will be delayed; thus the phenomenon of ST occurs only under a high shear rate.

Acknowledgments

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