

Effect of Carbon Particles with Different Topological Shape on the Rheological Behavior of PVA Aqueous Dispersion

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Abstract Poly(vinyl alcohol) (PVA) is usually processed and used in a form of aqueous dispersion. A large number of inter- and intramolecular hydrogen bonds make it very difficult to obtain suitable rheological behavior for processing. In this study, carbon particles with different topological shapes were added into PVA aqueous dispersion to tune the steady and dynamic rheological behavior. The results show that the zero-dimensional particles (carbon black, CB) increase monotonically the zero-shear viscosity of PVA dispersion, while the one-dimensional particles (carbon nanotubes, CNTs) make it first increase, and then decrease and rise again, like an N-shape, and the two-dimensional particles (graphene oxide, GO) can make it first decrease and then increase, exhibiting a U-shape. It is believed that the topological shape of the carbon particles brought about these discrepancies. The zero-dimensional particles mainly act as physical crosslinking points due to their small size. While at a certain content, both CNTs and GO can destroy the intermolecular hydrogen bonds between PVA chains because the PVA chains can twine around the slim CNTs and the large planar size of GO prevents the adsorbed PVA from forming hydrogen bond with other chains. The high hydroxyl value of carbon particle surface could strengthen this effect. It is expected that the viscosity of polymer dispersion can be regulated by particles with different topological shape and the surface characteristic, so as to widen the operable concentration range during preparing composite functional materials.

Keywords Topological shape; Hydrogen bond; Rheological behavior; PVA aqueous dispersion

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INTRODUCTION

Poly(vinyl alcohol) (PVA) is one of the first synthetic polymers to be produced on a large scale commercially and has been utilized in various applications, including hydrogel for biomaterials, fibers for clothes, films, membranes, matrix for drug delivery systems, emulsifier and stabilizer for colloid suspensions, sizing agent and coating in textile and paper industries, and so on.^[1–8] In most cases, PVA is processed and used in a form of aqueous dispersion. To realize the diverse industrial applications as mentioned above, it is important to regulate the rheological behavior of PVA aqueous dispersion, and thus optimize the processing technology as well as the performance of PVA products.^[7,9,10] The side hydroxyl groups in PVA chains could form strong inter- and intra-molecular hydrogen bonds, which has a pronounced effect on the rheological behavior of PVA aqueous dispersion. Although many studies have explored the influence of hydrogen bonds

on the crystal structure of PVA,^[11–13] there are only a few studies on the rheological behavior of PVA aqueous dispersion.

Incorporating inorganic and organic particles has been widely used as a low cost route to improve the performance of the polymer products. Particles are often added to endow the final polymer products (such as electrode membrane, conductive film, antimicrobial film, photoelectrocatalytic film, functional fiber, high-strength, high-modulus film, etc.) better physical and mechanical properties and functionality. These functional particles include carbon nanotubes (CNTs), SiO₂ particles, silver nanoparticles, nanometer titanium dioxide and other inorganic or metallic particles.^[14–17] In general, the addition of most particles increases the viscosity of the polymer solution, which has been proved by theoretical simulations and experiments.^[18] Chen *et al.* mixed nano-hydroxyapatite with PVA powder and found that the viscosity rose accordingly as the amount added went up.^[19] Otsubo *et al.* found that the rheological parameters of the PVA aqueous dispersion increased with the amount of CB particles.^[20] By contrast, only a few references reported particles can reduce the viscosity of polymer solution. For example, Tan *et al.* reported that graphene could control the viscosity of the PVA dispersion by changing the surface proper-

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ties,^[21] the reduced graphene oxide decreased the viscosity while the graphene oxide increase the viscosity of PVA dispersion. Nano attapulgite can decrease the viscosity of PVA dispersion in a case of low content (<5 wt%).^[22] In our previous studies, layered double hydroxide (LDH) nanoscrolls, an one-dimensional particle, reduce the viscosity of PVA dispersion at a certain content, while both the LDH nanosheets and microsheets increase the viscosity of the dispersion.^[23] The hydroxyl group on LDH particle surface can form hydrogen bonding with the side hydroxyl group of PVA chains. These results indicate that the rheological behavior of PVA dispersion can be tuned by the topological shape and surface properties of the particles.

In order to determine the universality of this phenomenon, we intend to explore how the addition of particles with different topological shapes affect the formation of hydrogen bond between PVA chains and the final rheological behavior of the system. Carbon-based particles with different shapes including zero-dimensional carbon black (CB), one-dimensional carbon nanotubes (CNTs) and two-dimensional graphene (GE) have attracted significant scientific and technological interest for their superior electrical, thermal and mechanical properties.^[24,25] In this study, the commercial carbon particles with different topological shape, CB, CNTs and GE, were chosen to add into PVA aqueous dispersion to study the influence of topological shape of the particles on the rheological behavior of PVA dispersion. We try to figure out the synergistic effect of topological shape and surface characteristic of particles in tuning the rheological behavior of polymer solutions.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA, analytically pure) was purchased from Sinopharm Chemical Reagent Co., Ltd., with a polymerization degree of 1750 ± 50 , alcoholysis degree of 98%–99%. Carbon black (CB) with an average diameter of 30 nm, was delivered from Longxing Chemical Co., Ltd. Carbon nanotubes (CNTs) were purchased from Shanghai Macklin Biochemical Co., Ltd., with the hydroxyl value of 1.8% and a purity of 95%. Graphene oxide (GO) purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. has a 40% of oxygen-containing functional groups and purity of 99%. Nitric acid was purchased from Sinopharm Chemical Reagent Co., Ltd., with the concentration of 68%. NaOH was purchased from Sinopharm Chemical Reagent Co., Ltd. with the purity of 96%. Deionized water (DI water) from a water-purification system was used through the experiments.

Surface Modification

Neat CB particles, containing only a small amount of O, H and other elements, are difficult to disperse homogeneously in water due to their strong conjugate structure. To improve the dispersion of CB in water, nitric acid was used to modify the CB particles surface.^[26] The CB particles with a weight of 1.5 g were mixed with 45 mL of 68% nitric acid, ultrasonic surge for 30 min and then refluxed for 7 h at 373 K. After that, the samples were taken pumping filtration and drying and then sealed for subsequent testing. The obtained product is denoted as

oxidized CB (OCB).

Preparation of Composite Aqueous Dispersion

Take 10 wt% PVA aqueous dispersion with a mass fraction of 0.5 wt% OCB as an example, 0.025 g of OCB was added into 45 mL of deionized water and treated by ultrasonic for 30 min. Then, 5 g of PVA powder was introduced under stirring and heated to 366 K. After complete dispersion, the composite dispersion was naturally cooled to room temperature for subsequent testing.

Characterization

Hydroxyl value

NaOH (0.16 g) was added into 100 mL of demineralized water to prepare NaOH standard solution. Then, 0.20 g of OCB powder was added into 20 mL of deionized water, ultrasonic surge for 3 min. Finally, the hydroxyl value of OCB aqueous dispersion was measured with NaOH standard solution titration, and a titration process was tracked by a pH meter until the pH endpoint was close to 7. From the consumption of NaOH standard solution, the hydroxyl value was calculated.

Rheological behavior

The rheological behavior of PVA composite aqueous dispersion was measured by a DHR-2 rotary rheometer (TA company, USA). The plate fixture with a diameter of 40 mm was used for dynamic and steady-shear scanning test. The shear rate ($\dot{\gamma}$) ranged from 10^{-3} s^{-1} to 10^3 s^{-1} . The frequency (ω) range of dynamic scanning was $0.016\text{--}100 \text{ rad}\cdot\text{s}^{-1}$, and the strain (γ) was set as 2%, which was in a linear viscoelastic region. All the rheological tests were performed at 298 K.

Melting enthalpy

The melting enthalpy of the samples was obtained by a Q25 DSC instrument (TA, USA). composite dispersion (5–10 mg) was weighed and sealed in a liquid crucible, which was first lowered to 233 K and then heated to 313 K at a rate of 5 K/min to prevent the lag of thermal effect caused by too fast heating.

RESULTS

Morphology and Properties of the Carbon Particles

The morphologies of the three carbon particles are shown in Fig. 1. OCB particles are spherical, and the diameter is about 10–50 nm. CNTs exhibit thread shape, with a diameter of 10–60 nm and a length of several micrometer. Commercial GO particles have sheet shape with a size of $\sim 2 \mu\text{m}$ and thickness of several nanometer. Thus OCB, CNTs and GO are considered as zero-dimensional, one-dimensional and two-dimensional particles, respectively.

Fig. 2 shows the FTIR spectra of several carbon particles. The characteristic bands of oxygenated group at 3430 cm^{-1} (O–H stretching), $1590\text{--}1630 \text{ cm}^{-1}$ (C–OH bending) can be observed for OCB, but not in CB, reflecting more oxygenated groups, such as hydroxyl and carboxyl groups, have been formed on the surface of OCB after the treatment, which was expected to improve the dispersibility in water. These characteristic bands of oxygenated groups also appeared in GO and CNTs. Besides, the characteristic band of C=O stretching (1730 cm^{-1}) can be observed for GO particles.

The hydroxyl values of the three kinds of carbon particles were measured and summed in Table 1. After nitric acid treatment, the hydroxyl value of OCB is about 1%, which is close to

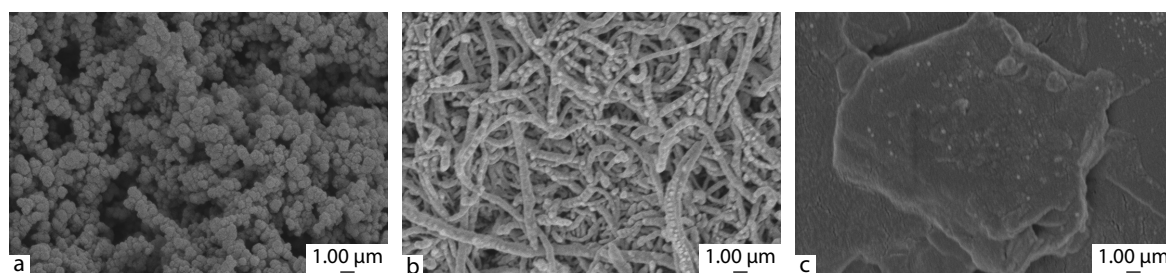


Fig. 1 SEM images of the carbon particles: (a) OCB, (b) CNTs, (c) GO.

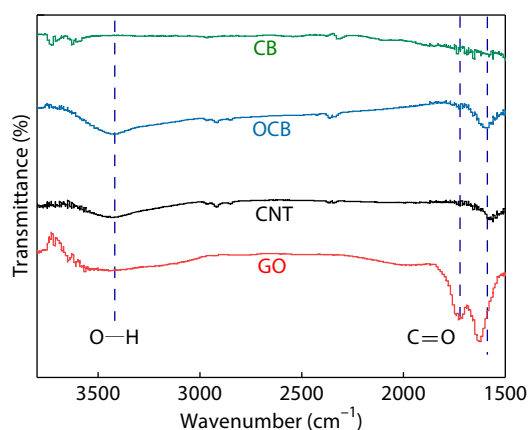


Fig. 2 FTIR spectra of different carbon particles.

Table 1 Hydroxyl values of different carbon particles.

Particle	Hydroxyl value (%)
OCB	1
CNTs	1.8
GO	40

that of commercial CNTs (1.8%). While the hydroxyl value of commercial GO sheet is as high as 40%. GO with relatively low hydroxyl value in water is poor, so this commercial GO with hydroxyl value of 40% was directly used.

Rheological Behavior of PVA/OCB Composite Dispersion

The steady and dynamic rheological behaviors of PVA/OCB dispersion with various OCB content (ϕ_{OCB}) are shown in Fig. 3. OCB is considered as a kind of zero-dimensional particles due to its small size. With increasing shear rate ($\dot{\gamma}$), the apparent

viscosity (η_a) of all the composite dispersions decrease, which is of typical shear thinning phenomena (Fig. 3a). Significant differences could be observed in the region of $\dot{\gamma} < 1 \text{ s}^{-1}$, while small difference in high $\dot{\gamma}$ region. The steady shear curve of neat PVA and the composite dispersion could be divided into four regions by three critical shear rate, $\dot{\gamma}_{c1}$, $\dot{\gamma}_{c2}$ and $\dot{\gamma}_{c3}$.^[27] The plateau at $\dot{\gamma} < \dot{\gamma}_{c1}$ is the first Newton region; $\dot{\gamma}_{c1} < \dot{\gamma} < \dot{\gamma}_{c2}$ is a region of shear thinning; while the plateau at $\dot{\gamma}_{c2} < \dot{\gamma} < \dot{\gamma}_{c3}$ is considered as the second Newton region. As we have known, the strong interaction between PVA chains favors forming network structure in which the intermolecular hydrogen bonding points act as the physical crosslinking points.^[27] During a simple shear with $\dot{\gamma}$, a certain structure begins to be destroyed when Weissenberg number $We = \tau\dot{\gamma}$ is close to one,^[28] where τ is the characteristic relaxation time that relates to a certain moving unit or structure. Thus, three characteristic relaxation time, $\tau_{c1} = 1/\dot{\gamma}_{c1}$, $\tau_{c2} = 1/\dot{\gamma}_{c2}$ and $\tau_{c3} = 1/\dot{\gamma}_{c3}$ were gained respectively. With the addition of OCB, $\dot{\gamma}_{c1}$ moves toward low $\dot{\gamma}$, while $\dot{\gamma}_{c2}$ moves to a high $\dot{\gamma}$ region.

The relationship between zero-shear viscosity (η_0) and ϕ_{OCB} was shown in Fig. 3(b). η_0 of the PVA/OCB composite dispersion were all larger than that of neat PVA dispersion and increases monotonously with ϕ_{OCB} .

Fig. 3(c) gives the dynamic rheological behavior of PVA/OCB composite aqueous dispersions. With the increase of ϕ_{OCB} , both the storage modulus (G') and loss modulus (G'') increase over the measured frequency (ω) range. Note that G' is higher than G'' at the low ω range, while G' is lower than G'' at the high ω range for neat PVA dispersion, which differs from the conventional polymer solution.^[29] Moreover, G' changes little with ω , just like a plateau. These phenomena may be caused by the network structure coming from the PVA intermolecular hydrogen bonds. The frequency at the in-

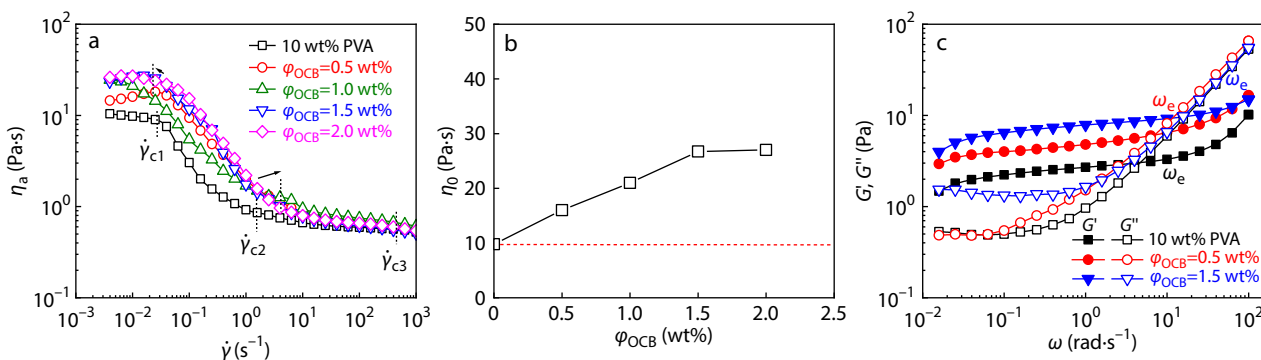


Fig. 3 Steady and dynamic rheological behavior of PVA/OCB composite dispersion with different ϕ_{OCB} (10 wt% PVA dispersion). (a) η_a versus $\dot{\gamma}$; (b) η_0 versus ϕ_{OCB} ; (c) G' and G'' versus ω .

tersection (ω_e) of G' and G'' , is 5 rad/s or so. According to the linear viscoelasticity theory, the plateau of G' and G'' actually means the reduction of dynamic viscosity (η^*),^[30] that is, the destruction of intermolecular hydrogen bonds in this system. Our previous research has revealed that $\dot{\gamma}_{c1}$ and τ_{c1} relates to the collapse of network structure formed through the intermolecular hydrogen bonding, while $\dot{\gamma}_{c3}$ or τ_{c3} corresponds to the relaxation of the overlap network structure of PVA chains (similar to unentangled semidilute PVA dispersion).^[31] The second plateau between $\dot{\gamma}_{c2}$ and $\dot{\gamma}_{c3}$ reflects that the overlap network structure are transient stable during this shear region. ω_e , being close to $\dot{\gamma}_{c2}$ not $\dot{\gamma}_{c1}$ of Fig. 3(a), is the endpoint of destroying the intermolecular network structure of PVA chains. Compared with the conventional polymer solution without strong intermolecular interaction in a state of entangled semidilute solution,^[29] the value of ω_e of PVA dispersion is relatively low, which may be due to the bound from the intermolecular hydrogen bond. The corresponding relaxation time τ_e ($\tau_e = 1/\omega_e$) of neat PVA dispersion is about 0.2 s. The modulus at ω_e could be considered as the plateau G_e of the overlap network structure. For neat PVA dispersion, $\omega_e = 4.7$ rad/s, and $\tau_e = 1/\omega_e \approx 0.2$ s. G_e at ω_e is about 3 Pa. Therefore, $G_e \tau_e \approx 0.6$ Pa·s, which is almost equal to the viscosity (0.62 Pa·s) of the second Newton plateau (Fig. 3a, $\dot{\gamma}_{c2} \sim \dot{\gamma}_{c3}$). This confirms again that the second plateau during the steady shear associates with the overlap network structure of PVA dispersion. With increasing ϕ_{OCB} , ω_e monotonically moves toward the large ω region and G_e move up, exhibiting the characteristic of enhanced network structure. This is consistent with the result of steady shear, i.e., $\dot{\gamma}_{c2}$ toward high $\dot{\gamma}$ with ϕ_{OCB} increase.

Rheological Behavior of PVA/CNTs Composite Dispersion

CNTs are widely used as a kind of one-dimensional particles. The steady shear curves of the composite dispersion with different CNTs content (ϕ_{CNTs}) were shown in Fig. 4(a). Still, the significant differences appear at the region of lower $\dot{\gamma}$. Different from the PVA/OCB composite dispersion, η_a of the PVA/CNTs composite dispersion with $\phi_{CNTs} < 0.5$ wt% is higher, while η_a of that with $\phi_{CNTs} > 1.0$ wt% is lower than that of neat PVA dispersion. For the $\phi_{CNTs} = 0.5$ wt% composite dispersion, $\dot{\gamma}_{c1}$ moves toward low $\dot{\gamma}$, and $\dot{\gamma}_{c2}$ shifts to high $\dot{\gamma}$, which consists with that of PVA/OCB composite dispersion basically. While for the $\phi_{CNTs} = 1.5$ wt%

dispersion, both $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$ move to low $\dot{\gamma}$. For polymer composites, high particle content usually leads to high η_a and short first Newton plateau.^[32] While the low η_a and the shorter first Newton plateau of PVA/CNTs composite dispersions with high ϕ_{CNTs} (such as 1.5 wt% and 2.0 wt%) may reflect the weakening of shear deformation resistance.

The corresponding η_0 versus ϕ_{CNTs} was shown in Fig. 4(b). In contrast to the PVA/OCB composite dispersion, η_0 of PVA/CNTs composite dispersions first increases ($\phi_{CNTs} < 0.5$ wt%), and then decreases ($0.5 \text{ wt}\% < \phi_{CNTs} < 1.5 \text{ wt}\%$) and rises again ($\phi_{CNTs} > 1.5 \text{ wt}\%$), showing an N-shape.

In order to confirm the abnormal rheological behavior, Fig. 4(c) shows the dynamic rheological behavior of PVA/CNTs composite dispersions with various ϕ_{CNTs} . G' and G'' of PVA/CNTs with $\phi_{CNTs} = 0.5$ wt% are larger than those of the neat PVA dispersion, being consistent with Figs. 4(a) and 4(b), in which the composite dispersion exhibits a higher η_a and η_0 . Its G' changes little over the most measured ω range. The corresponding ω_e moved to higher ω range and G_e increased compared with that of neat PVA dispersion. High G_e means dense overlap network structure and thus low τ_e . While the PVA/CNTs composite dispersion with $\phi_{CNTs} = 1.5$ wt% shows lower G' and G'' , and ω_e shifts to the lower ω and the G' plateau becomes narrower, implying that the adding of 1.5 wt% CNTs destroys the network structure to some extent. Because of the similar hydroxyl values of OCB and CNTs, the different topological shape of particles may cause the above distinct results.

Rheological Behavior of PVA/GO Composite Dispersion

Graphene is a kind of typical two-dimensional particles. Due to the strong van der Waals force between layers and π - π accumulation effect, graphene are usually tend to irreversible aggregate and precipitate in water, organic solvents and polymer matrix.^[33] Therefore, graphene oxide (GO) particles were used in this study. As given above, the hydroxyl value of the purchased commercial GO is as high as 40%, which is much higher than that of OCB and CNTs. Because GO particles with relatively low hydroxyl value are hard to dispersed homogeneously in water, this commercial GO was directly used.

The steady shear curve of PVA/GO composite dispersion with different GO content (ϕ_{GO}) was shown in Fig. 5(a). η_a of the composite dispersion with $\phi_{GO} < 0.5$ wt% is lower while η_a

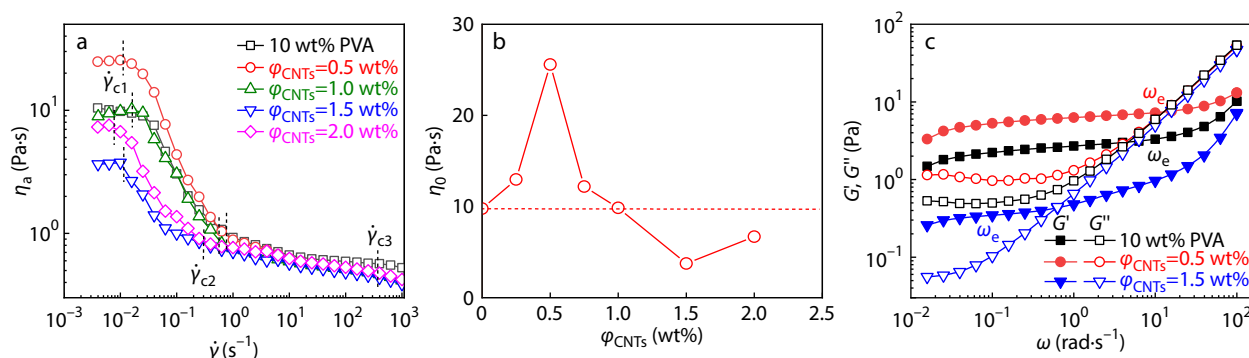


Fig. 4 Steady and dynamic rheological behavior of PVA/CNTs composite dispersion with different ϕ_{CNTs} (10 wt% PVA dispersion): (a) η_a versus $\dot{\gamma}$, (b) η_0 versus ϕ_{CNTs} , (c) G' and G'' versus ω .

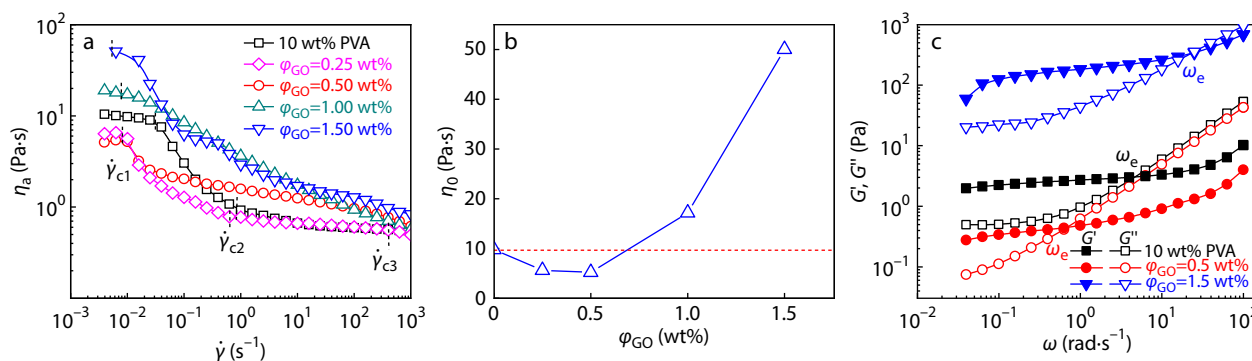


Fig. 5 Steady and dynamic rheological behavior of PVA/GO composite dispersions with different ϕ_{GO} (10 wt% PVA dispersion): (a) η_a versus $\dot{\gamma}$, (b) η_0 versus ϕ_{GO} , (c) G' and G'' versus ω .

of the dispersion with $\phi_{\text{GO}} > 1.0$ wt% is larger than that of neat PVA dispersion. Compared with the OCB and CNTs composite dispersions, the first Newton plateau of all PVA/GO dispersion shortens over the measured $\dot{\gamma}$ scope even in the case of low ϕ_{GO} . At $\phi_{\text{GO}} = 1.5$ wt%, the $\dot{\gamma}_{c1}$ moves toward low $\dot{\gamma}$ and the first and second Newton plateau almost disappear, along with the widening of shear thinning region, indicating that the intermolecular interaction are enhanced. This is due to the hydrodynamic interactions of individual particles in shear flow and particle-particle interactions coming from the larger volume fraction of GO particles. It brought the PVA chains more difficult to unentangle and the GO particles hard to orient, resulting in a higher shear rate for the emergence of the second plateau. The enhanced intermolecular interaction between macromolecular chains and particles as well as a stronger percolation network structure formed by the larger particles finally induce the higher η_a at high ϕ_{GO} , which is usually observed in most composite systems.

The η_0 of PVA/GO composite dispersions decreases first and then increases with ϕ_{GO} (Fig. 5b), which is different from Tan's report who found that the addition of GO particles increased the viscosity only and no decrease in low ϕ_{GO} , such as 0.5 wt%, was observed.^[21] The difference may originate from the different post-treatment method and the amount of oxygenated functional groups.

Fig. 5(c) shows the dynamic rheological behavior of PVA/GO composite dispersions. G' and G'' of 0.5 wt% GO composite dispersion are smaller, and ω_e shifts to low ω region and the G' plateau becomes narrower compared with the pure PVA dispersion, implying the weaker intermolecular network structure and the larger τ_e as well as the low G_e . While G' and G'' of PVA/GO with 1.5 wt% GO are much higher than that of pure PVA dispersion, and ω_e shifts to higher ω and the G' plateau becomes wider, which represents the strengthened intermolecular interaction between PVA chains.

DISCUSSION

From the steady shear curve of several PVA composite dispersions with different topological carbon particles, large difference in low $\dot{\gamma}$ region but little difference in high $\dot{\gamma}$ region was observed. η_0 of the PVA composite dispersions with the three different carbon particles is summarized in Fig. 6.

As mentioned above, the surface properties of the three

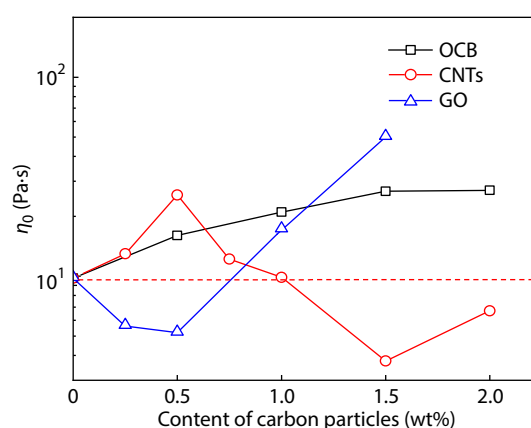


Fig. 6 η_0 of PVA composite dispersion with different carbon particles.

kinds of carbon particles are basically the same. It is supposed that the functional groups, such as hydroxyl and carboxyl groups, on these carbon particle surfaces can generate hydrogen bonding interactions with the side hydroxyl group of the PVA chains, making the PVA chains be adsorbed on the carbon particle surface. Therefore, the carbon particles should act as physical crosslinking points and increase η_0 of the PVA dispersion. The zero-dimensional particles OCB increase indeed monotonically the η_0 of PVA dispersion, while the one-dimensional particles CNTs make η_0 first increase, and decrease and then rise again, like an N-shape, and the two-dimensional particles GO make the η_0 first decrease and then increase, exhibiting a U-shape. It is considered that the topological shape of the carbon particles brings about these discrepancies.

Difference in topological shape generates various macromolecular adsorbed state on the particle surfaces. In order to deeply understand the above phenomenon, the adsorption states of PVA chains on these carbon particles with different topological shapes were figured out. We assume that a PVA chain is an ideal random coil with N minimum motion chain element, the average length of each chain element is a , and the average length (R_0) of PVA chain in a semi-dilute dispersion (a concentration of 10 wt%) is approximately $aN^{1/2}$. In this case, $R_0 \approx 16$ nm. The thickness of the compact adsorption layer of the macromolecular chain on the carbon particle surface was also defined as a for simplicity. The loss of free en-

ergy of a PVA unit chain on the surface of carbon particles was defined as ϵkT , and the change of free energy (F) of a polymer adsorbed on the surface of carbon particles only considering the van de Waals interaction is as follows:[34]

$$F = kT(R_0/D)^2 - \epsilon kTNf \quad (1)$$

where k is Boltzmann's constant, T is the Calvin temperature, D is the limited thickness of the molecular chain, ϵ is a constant related to the adsorption strength, and f is the percent of the chain element tightly attached to the particle surface. For the adsorption on a planar surface (like GO), f can be calculated from the following equation:

$$f \approx a/D \quad (2)$$

The minimum free energy can be obtained by substituting Eq. (2) into Eq. (1) and differentiating it. Then $D = 2a/\epsilon$ is obtained. Generally, the value of a is about 0.5 nm, and the adsorption constant of van der Waals force ϵ is 0.1, so D on the GO surface (D_{GO}) is approximately 10 nm. For long cylinders of radius b (like CNTs), f can be expressed as follows:[35]

$$f \approx 2ba/[(b+D)^2 - b^2] \quad (3)$$

By replacing Eq. (3) with Eq. (1) and minimizing the free energy, D on the CNTs surface (D_{CNTs}) can be obtained. D_{CNTs} is estimated to be about 10.3 nm.

For a spherical particle of radius b (like carbon black), f can be expressed as follows:[35]

$$f \approx 3b^2a/[(b+D)^3 - b^3] \quad (4)$$

By replacing Eq. (4) with Eq. (1) and minimizing the free energy, D can be obtained. D on a spherical particle with a radius of 15 nm (D_{OCB}) is estimated to be about 12.8 nm.

Herein, $D_{OCB} > D_{CNTs} > D_{GO}$ is obtained, implying that PVA chains form thicker adsorption layer on the OCB surface compared with CNTs and GO in the case of similar surface properties. Except for the van de Waals interaction, there are stronger interaction between carbon particles and PVA chains through hydrogen bonding, which might further decrease D . The adsorption fraction f of PVA chains on the surface of carbon particles with different shapes could be estimated by Eqs. (2), (3) and (4) as shown in Table 2. Large f implies high adsorption energy to some extent.

Based on the above analysis, the adsorbed states of PVA chains on the carbon particle surfaces with various topological shapes are determined. Schematic descriptions of PVA chains on different particle surfaces (Fig. 7) were given to account for the uncommon dependence of rheological behavior on the particle content.

In zero-dimensional particle filled system, the adsorption capacity (N^*) of an OCB particle was given by:[35]

$$N^* \approx (b/a)^2 \quad (5)$$

where b is 15 nm for OCB, a was 0.5 nm or so, then $N^* \approx 900$ is obtained. N of PVA used in this study is about 1700, namely

$N \approx 2N^*$. This indicates only a part of the macromolecule is adsorbed on the OCB particle surface with the rest attaching to other particles or chains, and thus the OCB particles are tendentially acted as chain bridging as shown in Fig. 7. That is, due to its small size, OCB particles can only adsorb a part of PVA chains and therefore primarily act as physical crosslinking points.

For one-dimensional particle filled system, Monte Carlo simulation results have demonstrated that the flexible polymer chains present cloud conformation when interact with a cylindrical surface.[36] In such a condition, loops which are prone to entangle with free chains than tails become more frequent, and lead to an enhanced friction effect for PVA/CNTs system at low ϕ_{CNTs} . With increasing ϕ_{CNTs} , chain adsorptions become predominant and PVA chains prefer to wind around the one-dimensional CNTs (such as $\phi_{CNTs} = 1.0$ wt%) rather than participate in constructing global hydrogen bonding network, and thus lead to a dramatic reduction of η_0 (Fig. 7). With further increasing ϕ_{CNTs} , the rising again of η_0 should be attributed to the aggregation of CNTs with large specific surface energy and the distinct effect of hydrodynamics and steric hindrance.[37,38]

The above estimation results show that the adsorption state on CNTs and GO are similar. Although both the two particles decrease the viscosity of PVA dispersion at a certain content, CNTs system show the N-shape extend, while GO system show the U-shape. The difference is that low ϕ_{GO} cannot make viscosity increase even ϕ_{GO} as low as 0.25 wt% likely owing to the higher hydroxyl value (40%) than that of CNTs (1.8%). Unlike the slender surface adsorption area of the cylinder CNTs, GO sheet has a relatively large surface area. When one segment of PVA is adsorbed on the GO sheet surface, the large size of GO sheet prevents the adsorbed PVA chains from entangling with other chains as shown in Fig. 7 due to the steric hindrance. When the ϕ_{GO} is higher than 1.0 wt%, the bridging effect was dramatically enhanced due to the hydrodynamic effect from its large lateral size, leading to a prominent increase in viscosity.

As described in Fig. 3(a), if the first plateau of steady shear curve relates to the network structure formed through the intermolecular hydrogen bond, the relationship between its characteristic relaxation time, τ_{c1} , and η_a is:

$$\tau_{c1} = \frac{\eta_a}{E} \quad (6)$$

where E is the Young's modulus of the network structure. E can be gained based on the mesh size of the network (ξ_H):[31]

$$E \approx \frac{kT}{\xi_H^3} \quad (7)$$

Then ξ_H is:

$$\xi_H \approx \left(\frac{\tau_{c1} kT}{\eta_a} \right)^{1/3} \quad (8)$$

τ_{c1} is 42 s or so, then ξ_H is calculated as 260 nm for neat PVA dispersion. In the light of literature,[39] only 5% hydroxyl groups could form intermolecular hydrogen bonds and act as physical crosslinking point. $\xi_H/R_0 \approx 16$, implying that there are about 16 PVA chains between the crosslinking points. From the dynamic frequency scan curve of Fig. 3(c), the chain with N_e units relaxes according to the Rouse mode with τ_e ,

Table 2 Adsorption thickness D and adsorption fraction f of PVA chains on various carbon particles.

		D (nm)	f (%)
CB	$f \approx 3b^2a/[(b+D)^3 - b^3]$	12.8	1.9
CNTs	$f \approx 2ba/[(b+D)^2 - b^2]$	10.3	3.6
GO	$f \approx a/D$	10	5

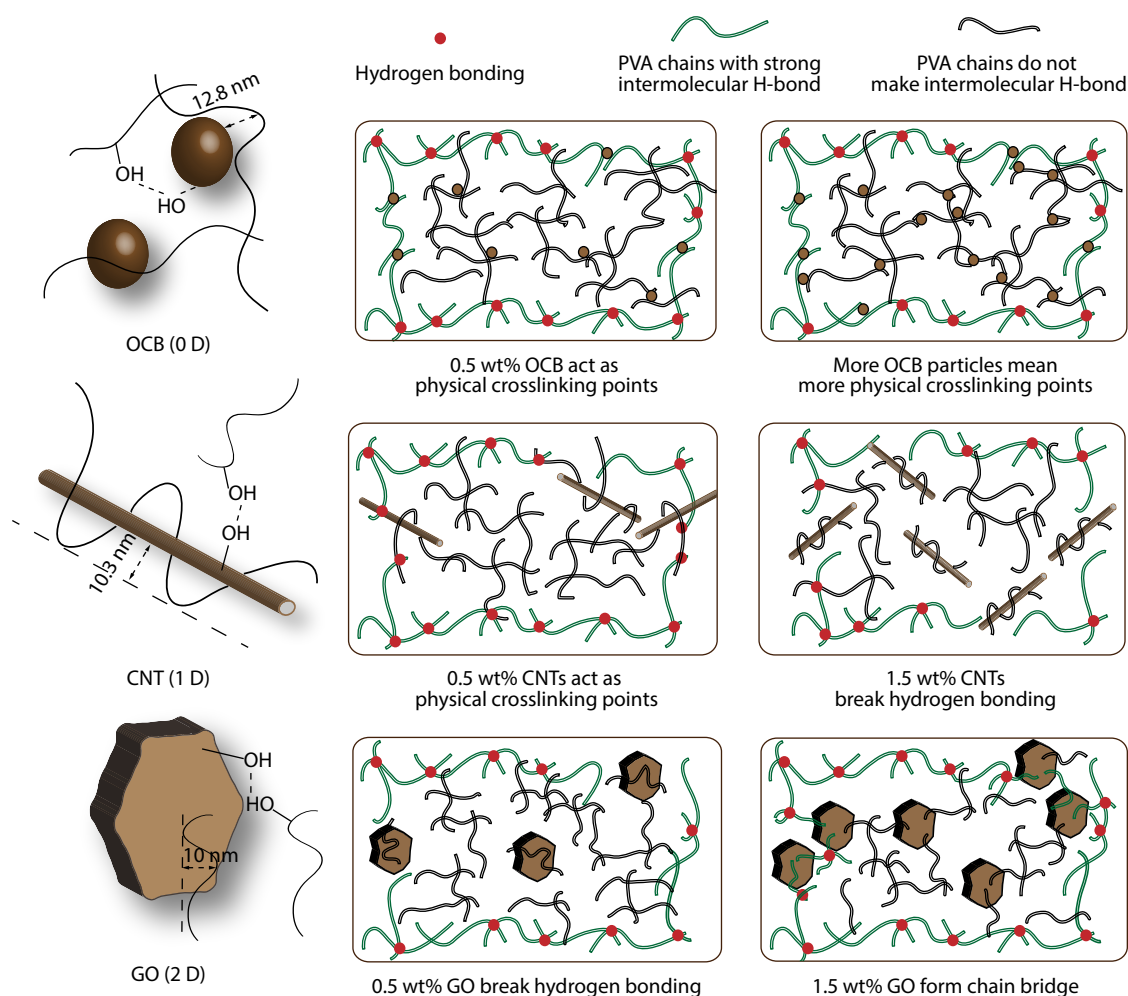


Fig. 7 Schematic diagram of PVA chains adsorbed on CB, CNTs and GO.

and $\tau_e = \tau_0 N_e^2$,^[31] where τ_0 is the relaxation time of Kuhn unit, accordingly, $N_e \approx 6.6 \times 10^4$. Then, $N_e/N \approx 39$ is obtained, which is larger than 16. This agrees with that ω_e (or τ_e) is close to the endpoint of destroying intermolecular network structure of PVA chains ($\dot{\gamma}_{c2}$).

As for OCB/PVA composite dispersion, we can see that the $\dot{\gamma}_{c1}$ moves to the lower $\dot{\gamma}$ with the addition of OCB. By applying Eq. (8), ξ_H of 0.5 wt% and 1.5 wt% OCB composite system can be estimated as 210 and 183 nm respectively which is smaller than that of pure PVA dispersion. The addition of OCB enhances the intermolecular interaction and reduces the mesh size between the crosslinking points. ω_e and $\dot{\gamma}_{c2}$ gradually moves towards the high frequency region with ϕ_{OCB} increase, leading to the widened shear thinning region.

For PVA/CNTs composite dispersion, ξ_H is estimated to be 240 nm for $\phi_{CNTs}=0.5$ wt%, being smaller than that of pure PVA system. This result is consistent with dynamic test of Fig. 4(c), in which the dispersion with lower ϕ_{CNTs} (0.5 wt%) presents the larger ω_e . It suggests that, just like OCB, a small amount of CNTs can act as physical crosslinking points and thus reduce the mesh size in the system. When ϕ_{CNTs} rises to 1.5 wt%, $\dot{\gamma}_{c1}$ and $\dot{\gamma}_{c2}$ shift to lower $\dot{\gamma}$, and the ξ_H is obtained as 420 nm, which is larger than that of neat PVA dispersion, meaning that the intermolecular network structure become

loose and η_a decrease. In this case, more PVA chains twin around CNTs and weakens the intermolecular interaction among PVA chains. A let-up of intermolecular interactions usually leads to a large $\dot{\gamma}_{c1}$.^[40] While in 1.5 wt% PVA/CNTs composite dispersion, the existence of CNTs with large ratio of length and diameter hinders the relaxation of PVA chains and thus extends the relaxation time to some extent. Both the decreased interparticle distance (larger ϕ_{CNTs}) and weaker interaction with the bulk polymer solution led to some CNTs aggregates, which may decrease $\dot{\gamma}_{c1}$.^[41] Attributing to the breakdown of intermolecular hydrogen bond, the shear thinning region is shortened, i.e., $\dot{\gamma}_{c2}$ moves to low $\dot{\gamma}$. The dynamic frequency scan test also demonstrates that ω_e moves to the lower frequency region (Fig. 4c).

To confirm the hydrogen bonding interaction between CNTs and PVA, hydration number (n), which is usually used to quantitatively describe the amount of bound water in each PVA repeating unit, was calculated. n can be determined by,^[42]

$$n = \left[\left(1 - \frac{\Delta H_m}{\Delta H} \right) \frac{1}{\bar{c}} - 1 \right] \frac{M_0}{M_{H_2O}} \quad (9)$$

M_{H_2O} and ΔH are the molecular weights and melt enthalpy of pure water, respectively. M_0 is the molecular weight of PVA

repeating unit, ΔH_m is the melting enthalpy of dispersion, c is the concentration of the PVA dispersion. n of 10 wt% neat PVA dispersion is 3.25, and n of PVA/CNTs composite dispersion with different φ_{CNTs} are shown in Fig. 8. With φ_{CNTs} increases, n decreases monotonously, meaning that the number of free hydroxyl groups bonded with water on the PVA chains decreases, and a part of the hydroxyl groups on PVA chains form hydrogen bond with the hydroxyl groups of the CNTs. In the case of low φ_{CNTs} , n decrease slightly, only a small amount of hydroxyl groups of PVA forms hydrogen bond interaction with CNTs, and thus CNTs mainly act as physical crosslinking points and increase the η_0 . As φ_{CNTs} increased, more hydroxyl groups of PVA chain form hydrogen bond with CNTs, the intermolecular interaction of PVA chains are destroyed, thus η_0 decreases. With φ_{CNTs} further increases, the aggregations of CNTs lead to the rise of η_0 again.

To explore the influence of particle surface characteristic on the rheological behavior, the CNTs with a hydroxyl value of 5.6% was introduced into PVA dispersion and the η_0 - φ_{CNTs} curve is shown in Fig. 9. With the increase of hydroxyl value, the η_0 - φ_{CNTs} curve moves toward low φ_{CNTs} and the minimum of η_0 decreases, indicating that the high hydroxyl value strengthens the interaction with PVA chains and let more PVA chains twine around the CNTs. There is a synergistic effect between topological shape and surface characteristic of

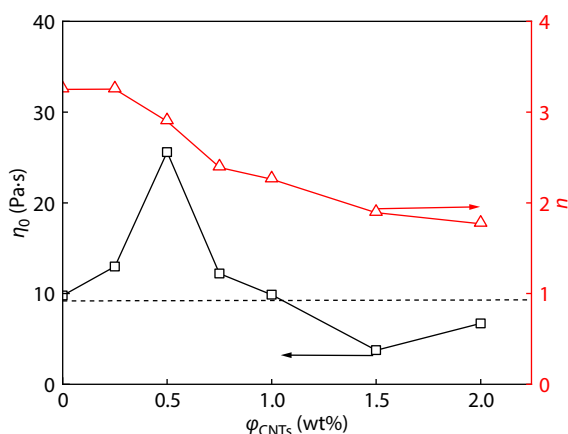


Fig. 8 η_0 and the hydration number of PVA/CNTs aqueous dispersion with different φ_{CNTs} .

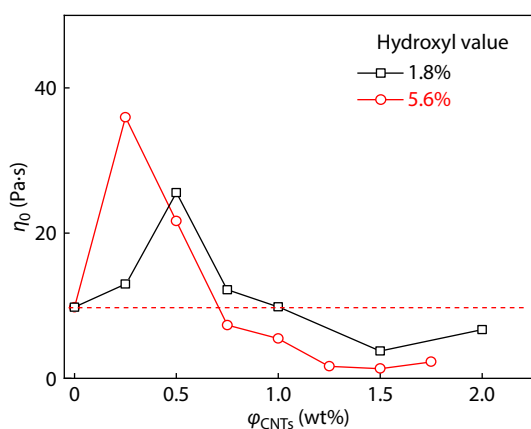


Fig. 9 η_0 of PVA/CNTs aqueous composite dispersion with different φ_{CNTs} and hydroxyl values.

particles in tuning the rheological behavior of polymer solutions.

For GO/PVA composite dispersion with $\varphi_{\text{GO}} = 0.5$ wt%, $\xi_H \approx 430$ nm, which is larger than that of neat PVA dispersion. As for GO/PVA composite dispersion with high φ_{GO} , $\dot{\gamma}_{c2}$ even disappeared, reflecting the enhanced intermolecular hydrogen bonding interaction. For GO/PVA composite dispersion with $\varphi_{\text{GO}} = 1.5$ wt%, ξ_H is estimated as 200 nm, being smaller than ξ_H of pure PVA dispersion. The dense intermolecular network structures together with the poor dispersion of GO sheets lead to a wide shear thinning region.

CONCLUSIONS

The carbon particles with different topological shapes influence remarkably on the steady and dynamic rheological behavior of PVA aqueous dispersion. The zero-dimensional particles OCB primarily act as physical crosslinking points due to their small size and the η_0 of PVA dispersion increases monotonically with φ_{OCB} . The one-dimensional particles CNTs act as physical crosslinking points at extremely lower φ_{CNTs} and high φ_{CNTs} , while CNTs could destroy the intermolecular interaction between PVA chains at a certain scope of φ_{CNTs} coming from their slim shape (large length/diameter ratio) and the interaction with polymer chains, and high hydroxyl value could strengthen the role. This makes η_0 of the composite dispersion first increase, and then decrease and increase again with φ_{CNTs} , like an N-shape. The two-dimensional particles GO could destroy the intermolecular interaction among PVA chains at low φ_{GO} because the large planar size of GO sheet prevents the adsorbed PVA from forming hydrogen bond with other chains, while act as physical crosslinking points only at a large φ_{GO} . This makes the η_0 first decrease and then increase, exhibiting a U-shape. It is expected that the viscosity of the polymer dispersion can be regulated by particles with different topological shape and the surface characteristic, so as to widen the operable concentration range in the preparation of composite functional materials.

NOTES

The authors declare no competing financial interest.

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