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High stability, high solid content, low viscosity titanium dioxide dispersion

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Abstract Achieving stable dispersion of titanium dioxide (TiO_2) particles is crucial for their practical applications in various fields. However, stabilizing pigment TiO_2 (200–300 nm) in aqueous systems with low viscosity (~ 10 cP) presents a significant challenge. In this work, we proposed a simple strategy using dispersant Disuper S9100 as dispersant and polyethylene glycol (PEG) as wetting agent to achieve single-dispersed TiO_2 particles with long storage stability and good re-dispersibility in low viscosity systems. The effect of PEG average molecular weight on the stability and re-dispersion performance of TiO_2 dispersion was investigated. Our study showed that PEG molecules were adsorbed on the surface of TiO_2 particles through hydrogen bonding, and synergized with nonionic polymeric dispersant Disuper S9100 to increase the steric hindrance between the particles. Due to the different adsorption conformations of PEG molecules, the dispersion stability and re-dispersibility of TiO_2 particles was gradually improved with increasing PEG average molecular weight. However, PEG molecules with excessively high molecular weight weakened the dispersion stability of TiO_2 particles. Overall, our findings suggest that the proposed strategy offers a promising approach to achieving stable TiO_2 particles in low viscosity systems.

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Introduction

Titanium dioxide (TiO_2) as a white pigment has a very wide range of applications due to its unique physical and chemical properties.[1–5] To achieve a sufficiently high coverage and whiteness, the particle size of the pigment TiO_2 is preferably about 200–300 nm, especially for applications such as painting, ink, and cosmetics.[6,7] Because of large particle size, high density and surface energy, TiO_2 particles are particularly prone to aggregation and sedimentation, which can seriously affect their application performance, especially in low viscosity systems like inkjet printing ink. Therefore, it is necessary to modify the surface of TiO_2 particles in order to achieve a stable dispersion and ensure good application performance. The key issue is to choose an appropriate modifying agent and modification method.

So far, surfactant adsorption and surface modification are the most widely applied methods to reduce the surface energy and to form a protective boundary preventing inter-particle adhesion.[8–11] Poly(acrylic acid)-based dispersants were investigated and utilized to achieve an efficient dispersion of TiO_2 by electrosteric stabilization in water-based paint. However, the high molecular weight of PAA led to increased viscosity and flocculation.[12–14] An alternative way to realize the good dispersion of large TiO_2 nanoparticle is to conduct the surface modification in order to increase the particle dispersion stability. López-Zamora et al.[15] used 3-aminopropyltriethoxysilane (APTES) as coupling agent to modify the surface of TiO_2 particles, and the dispersion stability of modified titanium dioxide particles in aqueous solution was significantly improved. However, due to the short chain segment of silane coupling agent, it is difficult to maintain the long-term dispersion stability of large particle size TiO_2 particles in water. Guo et al.[16] grafted polymethylhydrosiloxane (PMHS) on the surface of TiO_2 to obtain modified TiO_2 with good hydrophobic properties, which could be well dispersed in aqueous solution even at a high solid concentration with the aid of dispersants. Although the TiO_2 aggregation was effectively reduced due to steric hindrance, the strong hydrophobicity of the modified surface made the dried pigment difficult to be re-dispersed in water, ultimately limiting its long-term stability in aqueous systems. Very recently, Shen et al. reported a general strategy to monodispersity and stability of 200–300 nm TiO_2 particles in low viscosity systems. In the first step, a hydrophobic siloxane (PMHS) was grafted to the TiO_2 particle surface to prevent agglomeration of particles by the space steric hindrance of hydrophobic structure. Then a hydrophilic polyethylene glycol (APEG) layer was constructed to provide extra stability for the particle in aqueous systems. The modified dry powder (~ 250 nm) can be re-dispersed into water/glycol ethers solvent to form a single-dispersed suspension.[17] However, the two-step grafting process is relatively complicated and the as-prepared APEG-PMHS-R706s will form very hard lumps during the filtration process. Therefore, it is desired to develop a method to directly achieve monodispersity and stability of pigment TiO_2 particles dispersion with 200-300 nm particle size in low viscosity systems, especially the re-disperse capability of such nanoparticles in those systems.

In this work, we introduce a simple strategy using dispersant Disuper S9100 as dispersant and polyethylene glycol (PEG) as wetting agent to achieve single-dispersed TiO_2 particles with long storage stability and good re-dispersibility in low viscosity systems. The effect of PEG average molecular weight on the stability and redispersion performance of TiO_2 dispersion was investigated. The results showed that PEG can be adsorbed on the surface of TiO_2 particles through hydrogen bonding, and synergized with the nonionic polymeric dispersant Disuper S9100 to achieve single-dispersed TiO_2 particles with long storage stability and good re-dispersibility in low viscosity systems.

Materials and experimental methods

Materials

TiO_2 pigment with about 220 nm size (RDI-S) was obtained from Cansen Chemical (Shanghai) Co., Ltd. (Shanghai, China). Dispersant Disuper S9100, block copolymers containing amide groups was supplied by Guangzhou Core New Materials Technology Co., Ltd. (Guangzhou, China). PEG2000 (Average molecular weight 1800–2200, Purity ≥ 99.5%), PEG4000 (Average molecular weight 3600–4400, Purity ≥ 99.5%), PEG6000 (Average molecular weight 5400–7800, Purity ≥ 99.8%), and PEG8000 (Average molecular weight 7200–8800, Purity ≥ 99.0%) as wetting agents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). BYK-024 as defoaming agent was from BYK-Chemie GmbH (Shanghai, China). All the other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Preparation of TiO_2 dispersions

To prepare TiO_2 dispersions, dispersant Disuper S9100, BYK-024, deionized water and PEG with different molecular weight were respectively pre-dispersed by mechanical stirring for 30 min to obtain a mixture. The TiO_2 dispersions were prepared by ball milling. TiO_2 and as-prepared mixture were charged in jars at 40% w/w. Different-diameter ZrO_2 balls (2.5–4 mm) were added to each jar with a fixed mass ratio of 1:1 to the mixture. The jars were placed in the KS-370 disperser (Shanghai, China) and milled at a speed of 680 rpm at room temperature for 2 h. The resulting dispersion was then filtered using a 400-mesh filter cloth to remove ZrO_2 balls and insoluble impurities, followed by filtration using a 1.0 μm glass fiber filter membrane to obtain the S9100/PEG/RDI-S/H_2O dispersion containing wetting agent. The S9100/RDI-S/H_2O dispersion without PEG as wetting agent, the PEG/RDI-S/H_2O without Disuper S9100, and the RDI-S/H_2O dispersion without PEG and Disuper S9100 were used as the controls. The formulations of TiO_2 dispersions are listed in Table 1.

XPS measurement

X-ray photoelectron spectroscopy (XPS) spectra were obtained by Thermo Fisher Scientific K-Alpha High-resolution ultraviolet photoemission spectrometer.

Spectroscopy analysis

The dispersions were centrifuged and washed, dried and ground to obtain modified TiO_2 particles. An FTIR spectrometer (AVATAR 370, USA) was used to analyze the surface structure of bare and modified TiO_2 particles in the transmittance mode.

A transmission electron microscope (TEM) (JEM-CX200, Japan) was used to observe the dispersing state of TiO_2 particles in different dispersions.

Table 1: Formulations of TiO_2 dispersions

Composition	Content (wt%)						
	Dispersion 1	Dispersion 2	Dispersion 3	Dispersion 4	Dispersion 5	Dispersion 6	Dispersion 7
RDI-S	40.0	40.0	40.0	40.0	40.0	40.0	40.0
BYK-024	1.5	1.5	1.5	1.5	1.5	1.5	1.5
$C_2H_6O_2$	5.0	5.0	5.0	5.0	5.0	5.0	5.0
S9100	5.0	5.0	5.0	5.0	5.0		
PEG2000	/	1.5	/	/	/		
PEG4000	/	/	1.5	/	/	1.5	
PEG6000	/	/	/	1.5	/		
PEG8000	/	/	/	/	1.5		
H_2O	48.5	47.0	47.0	47.0	47.0	52	53.5

Surface tension test

In order to investigate the dispersion mechanism of TiO_2 particles, the surface tension of the mixed solution with different molecular weight PEG, corresponding to five dispersions (Dispersion 1–5 in Table 1) but without TiO_2 was tested at 25°C using automatic surface tension meter (KINO-A101, USA) with the platinum plate method.

The viscosity of the dispersions was measured using a Brookfield rotary viscometer at 25°C. The shear speed was 50 rpm.

Dispersion stability and re-disperse capability of dispersions test

The size contribution and polydispersity index of TiO_2 particles in the dispersion was analyzed by dynamic light scattering (Nanotrac Wave, Microtrac GmbH, Germany). After 7 days and 30 days, the size contributions of TiO_2 particles were taken to estimate the dispersion stability and re-dispersibility of the dispersions.

Settling behavior estimation

The settling behavior of TiO_2 dispersions was studied with a full-featured stability analyzer (LUMiSizer® 651, Germany), which measures the light intensity transmitted over their entire height as a function of time. The evolution of the transmission profiles during the centrifugation allows the quantification of dispersion stability and demixing phenomena. All measurements were carried out for a centrifugal acceleration with a speed of 3500 rpm at room temperature and transmission profiles were recorded every 10 seconds, with a light ratio of 1.0. Based on the transmission profiles, the values of instability indexes and settling rate in the spin field were calculated, and the phenomena of destabilization of dispersion systems were identified.

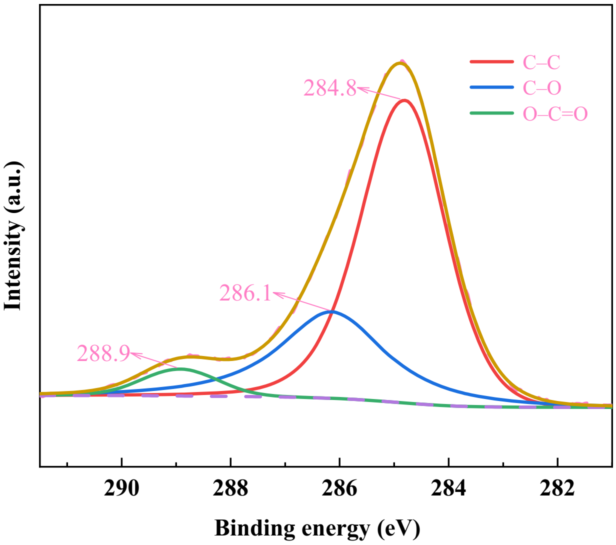

Fig. 1: High-resolution C 1s spectra of RDI-S

Results and discussion

Surface-modified TiO_2 particles

To render better paint formulations, the commercial TiO_2 particles might be modified with an inorganic and/or an organic layer. In order to better understand the physisorption process of PEG chains on TiO_2 nanoparticles, RDI-S particles were first characterized by XPS. XPS spectra (SI Fig. S1a) and high-resolution O 1s XPS spectra (SI Fig. S1b and S1c) showed that RDI-S particles were modified by Al_2O_3 and organosilicon. Importantly, besides Al_2O_3 and organosilicon, carboxylate groups might be used to modify the TiO_2 particles (Fig. 1). The isoelectric point of bare TiO_2 is 3 (SI Fig. S2), further confirming this point. In order to characterize the changes of functional groups on the surface of TiO_2 particles before and after modification with different wetting agents, the samples were characterized using FTIR. Figure 2 shows the FTIR spectra of the TiO_2 particles before and after interacting with different wetting agents. For the FTIR spectrum of RDI-S particles, the peaks at 1362 and 1610 cm^{-1} are

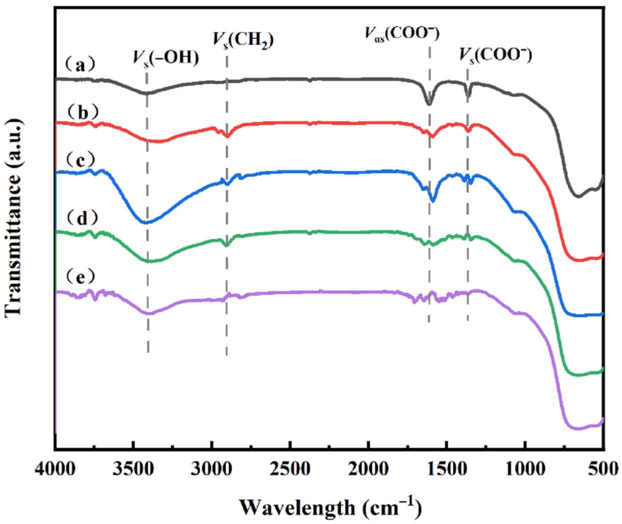

Fig. 2: FTIR spectra of TiO_2 particles before and after being modified with different wetting agents: (a) RDI-S, (b) PEG2000, (c) PEG4000, (d) PEG6000, (e) PEG8000

due to the symmetric and the asymmetric stretching vibrations of the carboxylate group, denoted as ν_{as}(COO$^-$) and ν_s(COO$^-$), respectively. The stretching vibration of the O–H bonds of carboxylate group gave rise to a broad peak at 3438 cm^{-1}, due to the intramolecular and hydrogen intermolecular bonding of carboxylate group.[18]

After modification with PEG of varying molecular weight, the peaks of ν_{as}(COO$^-$) and ν_s(–OH) blue-shifted (Figs. 2b–2e), which is attributed to the formation of hydrogen bonds between the ether bonds in PEG and O–H bonds in carboxylate groups of RDI-S particles.[19] Furthermore, curves b–e exhibit typical vibrational peaks of -CH$_2$- from the modifier PEG at 2889 cm^{-1}, and the intensity of the characteristic peak at 2889 cm^{-1} gradually increased with the increase of PEG molecular weight, further indicating that the PEG molecule was adsorbed on the surface of TiO_2 particles.[20,21]

TEM images of TiO_2 particles

The dispersion state and surface morphologies of TiO_2 particles were investigated by TEM, both before and after being modified in the dispersions. Figure 3 illustrates the effect of wetting agent type on the dispersion state of the TiO_2 particles. The ball-milled TiO_2 particles exhibited ellipsoidal morphology with an average size diameter of 220 nm, while TEM images revealed presence of aggregation of TiO_2 particles before adding wetting agent PEG. However, the addition of PEG improved the dispersion state of TiO_2 particles, as compared to unmodified TiO_2 particles. Interestingly, the overlap distance between TiO_2 particles first decreased and then increased with the increase of molecular weight of PEG. TiO_2 particles modified by PEG4000 in Fig. 3c had a better dispersion state compared with those modified by PEG2000, PEG6000 and PEG8000. This may be because the adsorbed PEG chains adopt a loop-and-train-tail conformation on the surface of the TiO_2 particles due to hydrogen bonds.[19,22] The theoretical study given by Simah demonstrated that for an adsorbed polymer on a solid surface showed three types of segment sequences, "trains" represent the adsorbed segments, "loops" represent the sequences of free segments connecting successive trains, and "tails" represent the nonadsorbed chain ends.[23,24] According to the study, the conformation of PEG adsorbed on the surface of TiO_2 particles may be related to the molecular weight of PEG, as shown in Fig. 4. Shorter PEG chains (PEG2000) adsorbed on the surface of TiO_2 particles formed trains conformation,[22] leading to a thin adsorption layer on TiO_2 particles with weak steric hindrance effect, thus failing to improve the dispersion performance significantly. Nevertheless, PEG chains with higher molecular weight formed Loops or Tails conformation. When the molecular weight of PEG exceeded 6000, mutual contact between PEG molecules adsorbed on the adjacent TiO_2 particles led to the formation of hydrogen bonds, causing poor dispersion through particle overlap.

Particle size distribution of TiO_2 particles

In order to investigate the effect of the type of wetting agent on the dispersion performance of TiO_2 particles, the particle size and its distribution of TiO_2 particles were determined by dynamic light scattering method. The size distributions of unmodified and modified particles with PEG in H_2O are plotted in Fig. 5. The particle size and the polydispersity index (PDI) are summarized in Table 2. According to the results, the unmodified TiO_2 particles showed a size ranging from D50 of 256 nm to D95 of 451 nm, and there were large particle clusters close to 1.0 μm in the dispersion, indicating severe agglomeration. Contrary to the unmodified TiO_2 particles, all PEG-modified TiO_2 particles with different molecular weight demonstrated a smaller average particle size and narrower particle size distribution. Especially, in the case of PEG4000 modification, D95 particle size decreased to 385 nm and the PDI was only 0.06. This indicated that the addition of the wetting agent PEG could promote the dispersion of TiO_2 particles. This could be attributed to the wetting effect, which facilitated the dispersion of TiO_2 particles in H_2O under the action of dispersant.

Viscosity of TiO_2 dispersions

Viscosity is a crucial factor considered in the applications of nanoparticle dispersion, especially in some fields like inkjet printing. The viscosity of TiO_2

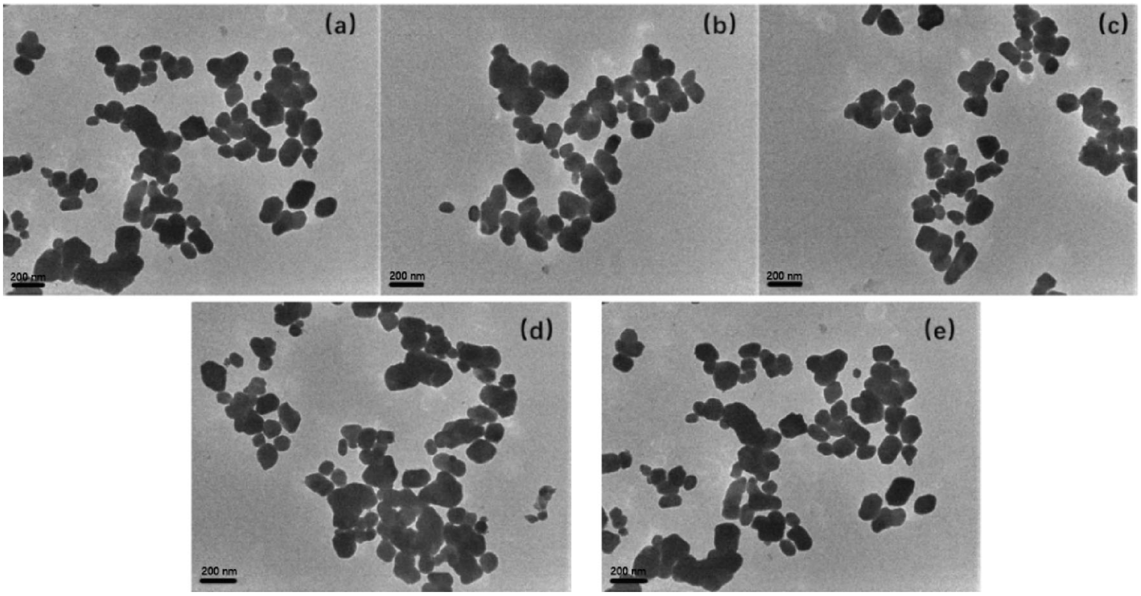

Fig. 3: TEM images of TiO_2 particles modified with different types of wetting agent: (a) No-PEG (Dispersion 1), (b) PEG2000 (Dispersion 2), (c) PEG4000 (Dispersion 3), (d) PEG6000 (Dispersion 4), (e) PEG8000 (Dispersion 5)

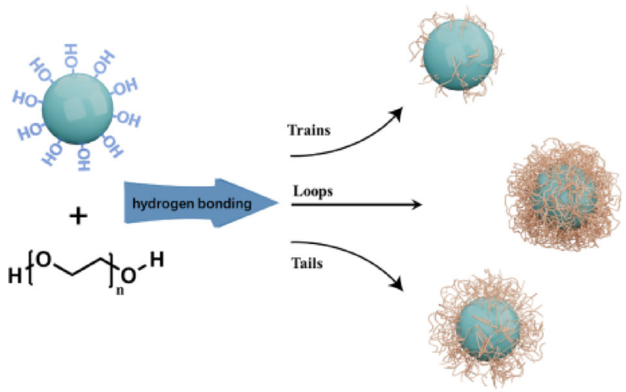

Fig. 4: The schematic diagram of the adsorption mechanism of PEG on the surface of TiO_2 particles

dispersions was tested. As shown in Fig. 6, the TiO_2 dispersions without dispersant Disuper S9100 had high viscosity. After adding dispersant Disuper S9100, all the TiO_2 dispersions exhibited very low viscosity, indicating the dispersant Disuper S9100 had excellent viscosity-reducing effect. Furthermore, when PEG was used as the wetting agent, the viscosity of the TiO_2 dispersions containing dispersant Disuper S9100 decreased from 12.63 to around 6.00 mPa·s. This is because the wetting effect of PEG molecules on the surface of TiO_2 particles can lower the surface free energy of TiO_2 particles, thereby promoting the adsorption of the dispersant on the TiO_2 particle surface. In addition, PEG adsorption on the surface of TiO_2 particles will increase the lubrication effect between particles, so the viscosity of the TiO_2 dispersion decreased significantly. It can also be seen from Fig. 6 that the viscosity of the TiO_2 dispersion with different molecular weight PEG was also different. With the increase of PEG molecular weight, the viscosity of the dispersion increased from 5.86 to 6.30 mPa·s. That could be explained by the resistance to the relative motion of TiO_2 particles due to the longer PEG chain, which led to the slight increase of the viscosity.

Dispersion stability and re-disperse capability of dispersions

A crucial factor hindering the widespread application of TiO_2 dispersions is the lack of dispersion stability and re-disperse capability, especially in low viscosity systems. When the dispersion has good dispersion stability and re-disperse capability, TiO_2 particles are not easily agglomerated. Even if TiO_2 particles are agglomerated, they are easily dispersed after slight shaking. Therefore, the particle size and its distribution basically remain unchanged. Thus, the average particle size and size distribution of TiO_2 particles in the dispersion were regularly tested to estimate the dispersion stability and re-disperse capability of dispersions (Fig. 7 and Table 3).

As can be seen from Fig. 7, there were particle clusters of more than 1.0 μm after 30 days of storage when no wetting agent was added or when PEG2000 was used as wetting agent. Using the higher molecular weight PEG as wetting agent, the size distribution of TiO_2 particles in the dispersion showed the lack of 1.0 μm clusters and the D50 decreased to less than 240 nm. Moreover, there was no significant increase in D50 after 30 days of storage. Initially, the D50 of TiO_2 particles in this dispersion was 239 nm; however, after

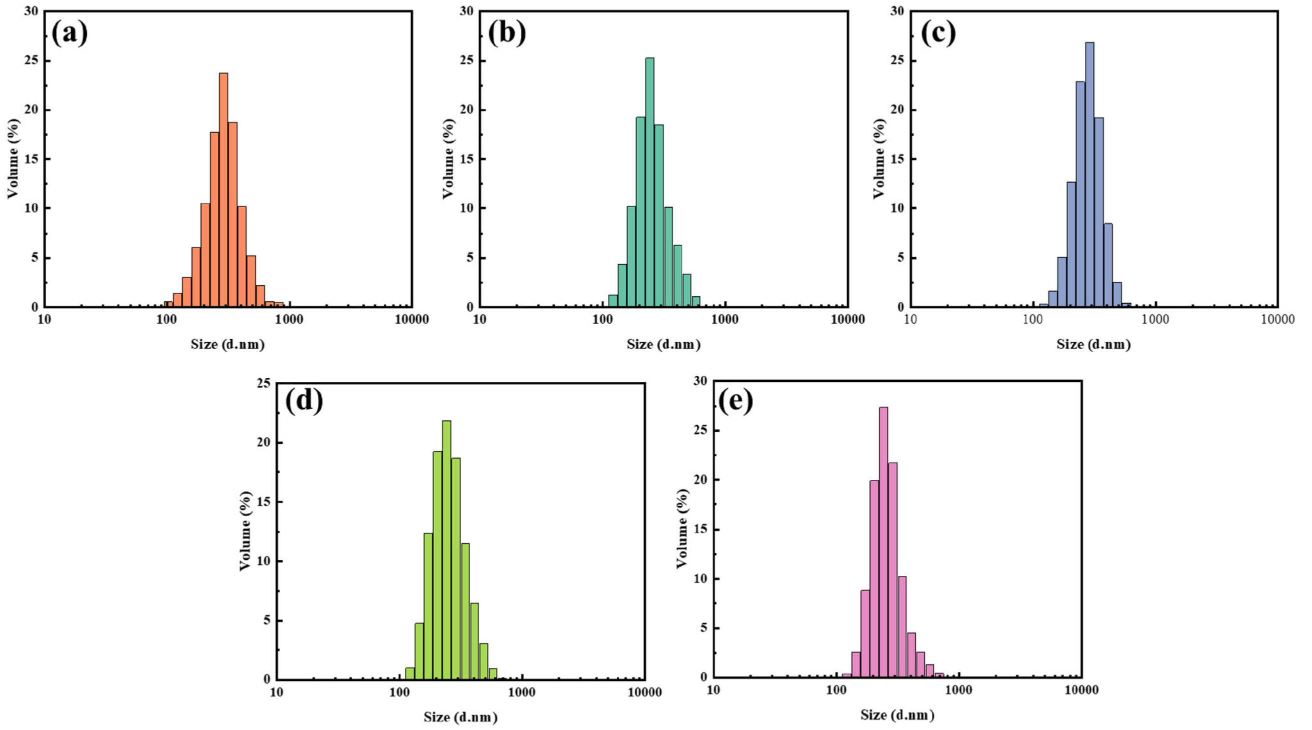

Fig. 5: Effect of wetting agent type on the particle size distribution of TiO_2 particles in dispersions: (a) No-PEG, (b) PEG2000, (c) PEG4000, (d) PEG6000, (e) PEG8000

Table 2: The particle size and polydispersity index of unmodified and modified TiO_2 particles using PEG with different molecular weight

Wetting agent	D_{50} (nm)	D_{95} (nm)	PDI
No-PEG	256 ± 11	451 ± 13	0.12
PEG2000	236 ± 8	403 ± 24	0.10
PEG4000	239 ± 6	385 ± 21	0.06
PEG6000	237 ± 8	397 ± 21	0.07
PEG8000	235 ± 10	395 ± 16	0.10

30 days of storage, it was only 247 nm. The D50 of TiO_2 particles varied within 10 nm, indicating that the dispersion had the best storage stability.

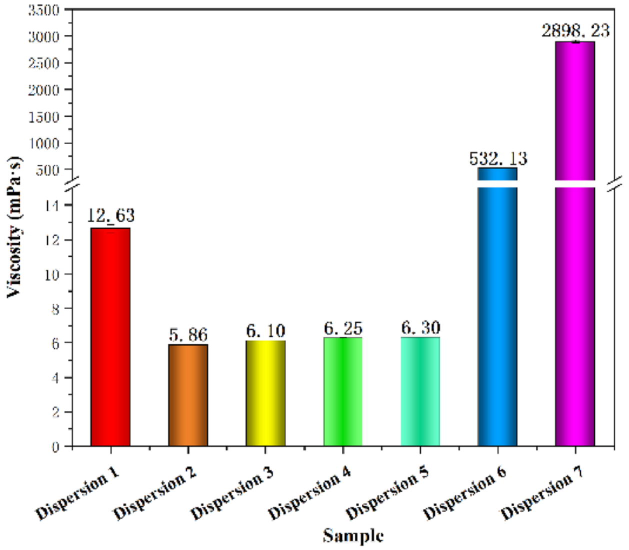

Fig. 6: Effect of wetting agent type on the viscosity of TiO_2 dispersions

Analysis of the settling behavior of dispersions

The settling characteristic of the dispersion is highly important and has a direct correlation to its stability. Understanding the settling characteristic is helpful for assessing the suitability of dispersions for their intended applications. Many studies are available on the settling of TiO_2 (< 50 nm) while few reports have focused on the large TiO_2 (200–300 nm).[25] It is needed to study the dispersion performance of it. The LUMiSizer® 651, a full-featured stability analyzer, was used to apply a certain gravitational acceleration to the dispersion and quantify changes in the concentration of TiO_2 particles in the local dispersion by testing the temporally and spatially dependent light projection intensity. The analyzer records the direction of light projection through the entire sample (from bottom to top) over a pre-selected period of time and detects any attenuation of incident light. When the sample is placed on the test bench and the centrifugal force is applied by LUMiSizer® 651, TiO_2 particles in

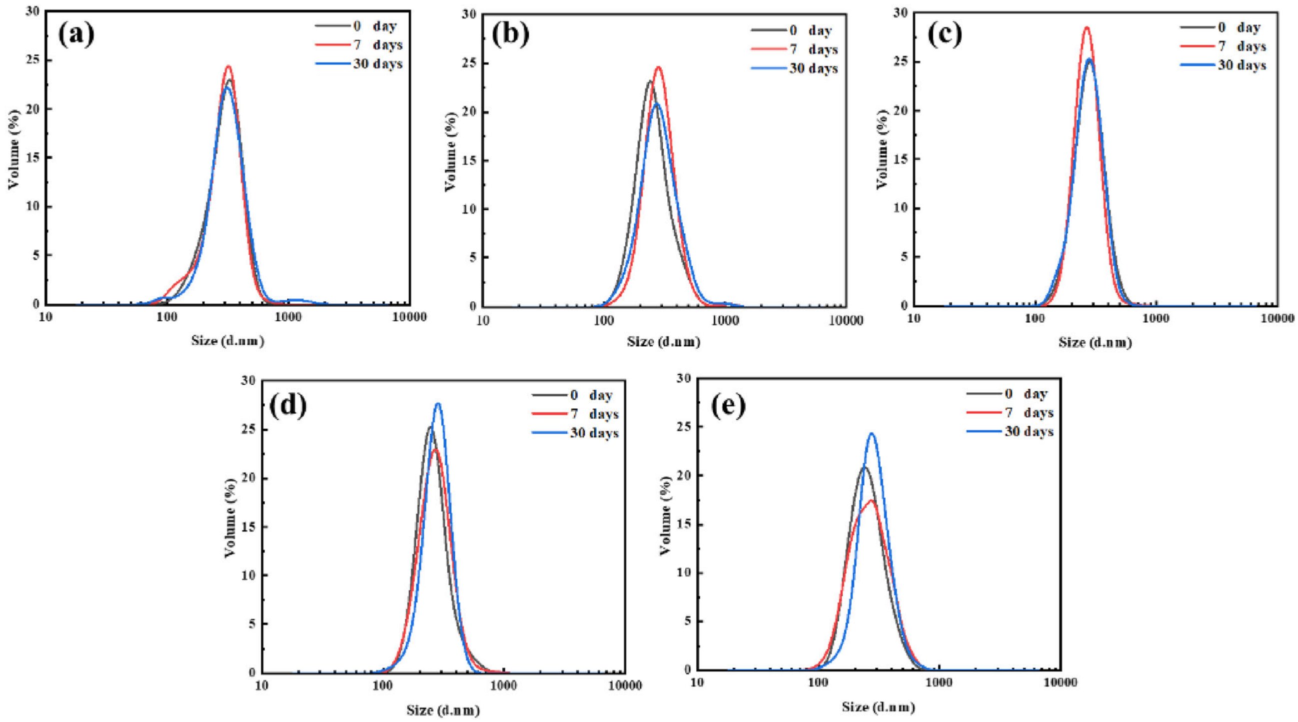

Fig. 7: Particle size distribution of TiO_2 particles in dispersions prepared with different wetting agents over 30 days: (a) No-PEG, (b) PEG2000, (c) PEG4000, (d) PEG6000, (e) PEG8000

Table 3: Variation of D_{50} of TiO_2 particles in different RDI-S/H_2O dispersions with time

Wetting agent	D_{50} (nm)		
	0 day	7 days	30 days
No-PEG	256	299	308
PEG2000	236	267	268
PEG4000	239	248	247
PEG6000	237	249	258
PEG8000	235	255	266

the dispersion will settle to the bottom of the sample bottle. The settling behavior of TiO_2 particles can be qualitatively analyzed by means of the transmittance-position profile.

The transmittance-position plot of the TiO_2 dispersion shows that the horizontal coordinates correspond to the position of the sample tube, with the top of the sample tube on the left and the bottom of the sample tube on the right, and the vertical coordinates represent the value of the transmittance of the sample, with the whole test proceeding from the beginning of the spectrum (red) to the end of the spectrum (green) over time. Since the original spectral line diagram had a total of 620 lines, the distribution was too dense to be easily observed, so five lines were selected for the diagram, as shown in Fig. 8.

As can be seen from Fig. 8a, the PEG-free TiO_2 dispersion showed the largest change in the test spectrum. The spectral lines are more broadly distributed in the early stage and more narrowly distributed in the later stage. The uneven changes indicated that the large particle clusters in the dispersion had priority to settle, followed by the sedimentation of small particles under the centrifugal effect; this is a typical step in the sedimentation process. After the addition of the wetting agent PEG, especially PEG4000 or PEG6000, the test spectrum of the dispersion presents uniform changes, and the overall slope of the spectral line is relatively gentle, which indicated that the TiO_2 particles in the dispersion settled slowly under centrifugal force. This is because the wetting agent can promote the dispersion of TiO_2 particles. There were no large particle clusters in the dispersion, and the particle size distribution was uniform, thus, no graded sedimentation took place. It was further proved that the addition of the wetting agent PEG could obviously improve the stability of the dispersion.

The instability index of the dispersion and the settling rate of TiO_2 particles in the dispersion for the first 1 h were further tested and the results are shown in Fig. 8. As seen from Fig. 9a, the dispersions settled completely after 8 h and the instability index no longer changed. It can be seen from Fig. 9b that the PEG-free TiO_2 dispersion showed a faster settling velocity and the settling rate of the dispersion decreased significantly after the addition of the wetting agent PEG to the dispersion. Furthermore, with the increase of the molecular weight of PEG, the settling rate exhibited a

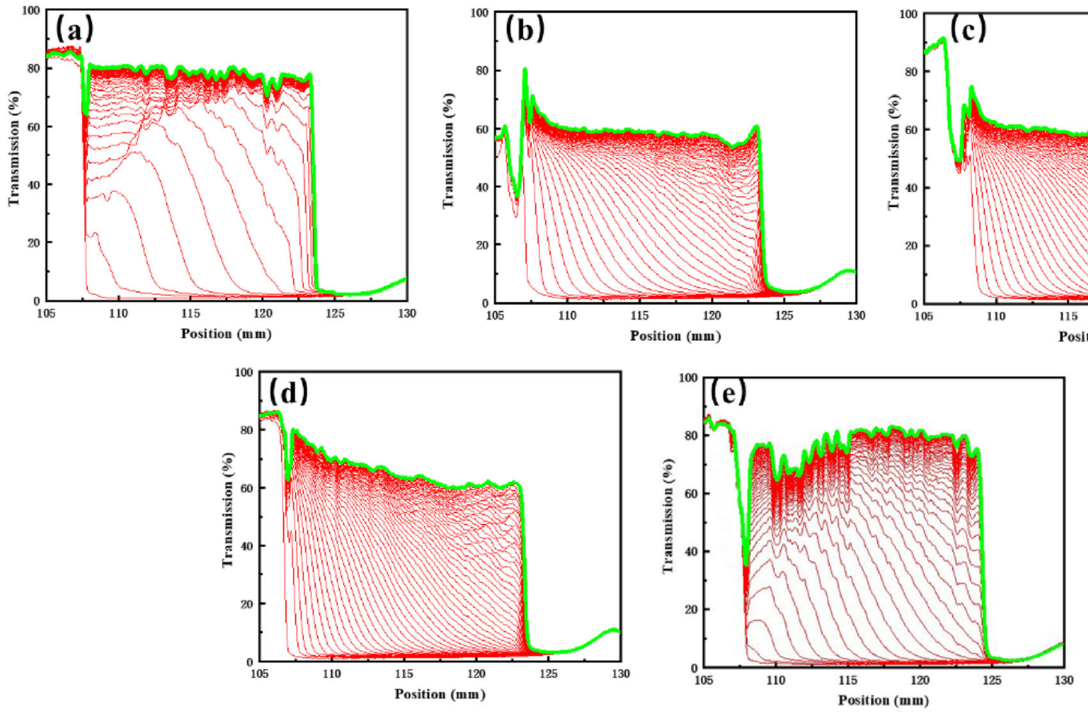

Fig. 8: Transmittance-position profiles of dispersions: (a) No-PEG; (b) PEG2000; (c) PEG4000; (d) PEG6000; (e) PEG8000 (Color figure online)

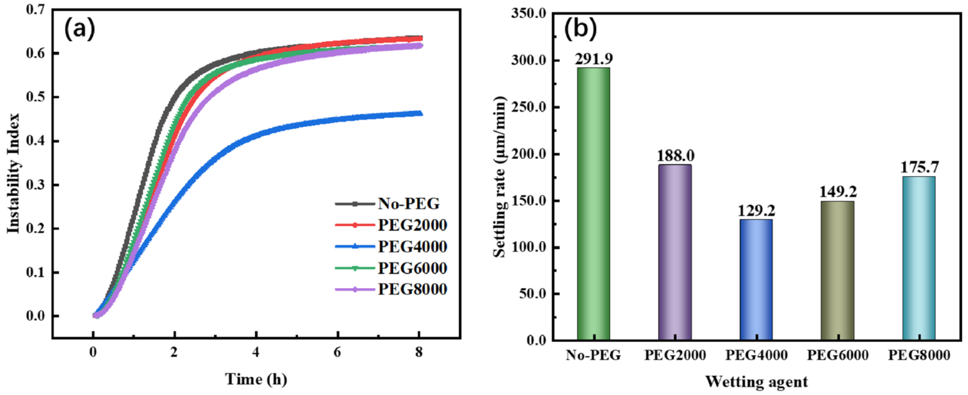

Fig. 9: (a) Dispersion instability index as a function of time, (b) effect of wetting agent type on the settling rate of the dispersion

trend of initially decreasing before subsequently increasing.

To further understand why the wetting agent PEG promoted the dispersion of TiO_2 particles, the surface tension of the mixed solutions corresponding to five dispersions (Dispersion 1–5) but without TiO_2 was tested and the results are shown in Fig. 10. The surface tension of the mixed solution without PEG was 51.32 mN/cm. After adding wetting agent PEG, the surface tension of the mixed solution decreased. When the molecular weight of PEG exceeded 4000, the surface tension of the mixed solution basically remained around 38 mN/cm. The lower the surface tension of the mixed solution, the more readily it could spread on the surface of TiO_2 particles, ultimately penetrating their clustered interiors and leading to improved wetting of TiO_2 particle surfaces. Once TiO_2 particles were completely wetted, the dispersant dissolved in the mixed solution could be better anchored on the surface of TiO_2 particles and achieved effective dispersion.

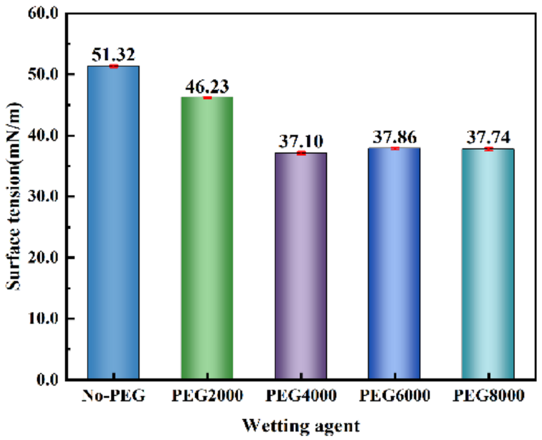

Fig. 10: Effect of wetting agent type on surface tension of mixed solutions

Conclusions

In this study, PEG was used for surface modification of pigment TiO_2 to improve the dispersion stability of TiO_2 in aqueous systems with low viscosity, and the effect of PEG molecular weight on the stability and re-dispersion performance of TiO_2 dispersion was investigated. PEG was adsorbed on the surface of TiO_2 particles through hydrogen bonding, and synergized with the nonionic polymeric dispersant Disuper S9100 to increase the spatial site resistance effect between the particles. Additionally, the surface tension of the solution decreased from 51.32 mN/cm to approximately 38.00 mN/cm after introducing PEG. This decrease in surface tension facilitated the spread and penetration of the solution on the TiO_2 particles surface, thus promoting the adsorption of dispersant and wetting agent and achieving the monodispersity of TiO_2 particles. The loops conformation formed after PEG4000 was adsorbed on TiO_2 particles surface was more conducive to increase the steric effect between particles, which could significantly improve the storage stability and re-dispersion performance of the dispersion.

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Conflict of interest The authors declare that they have no conflict of interest.

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