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DOE analyses on aqueous suspensions of TiO_2 nanoparticles

S. Baldassari[a], A. Bonamartini Corradi[b], F. Bondioli[b],
A.M. Ferrari[c,*], M. Romagnoli[b,*], C. Villa[a]

[a] *Dipartimento di Scienze Farmaceutiche, Università di Genova, 16132 Genova, Italy*
[b] *Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, 41100 Modena, Italy*
[c] *Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia, 42100 Reggio Emilia, Italy*

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Abstract

Nanosized titanium oxide (TiO_2) powders have been prepared by conventional and microwave hydrothermal methods by forced hydrolysis of $TiOCl_2$. As-prepared powders have been completely characterised by qualitative and quantitative XRD and TEM. The obtained titania powders have been redispersed (45 and 60 wt.%) in an aqueous hydroxypropylcellulose (HPC) solution (0.5–1 wt.%). Rheological characterisation has been performed in order to evaluate the influence of HPC on particles agglomerations. The effect of mixing time, HPC and TiO_2 concentration and their mutual interactions on shear stress have been evaluated with a design of experiment (DOE) approach.

Keywords: Nanoparticles; Hydroxypropylcellulose; Hydrothermal synthesis; TiO_2

1. Introduction

In recent years, nanosized titania has attracted substantial attention as a potential material in cosmetics, textiles, fine ceramics, photocatalysts for environmental purification, catalyst supports and dielectric materials, thanks to its unique physicochemical properties.[1–4]

Because of the technological importance of titania nanoparticles, different approaches to their synthesis such as chemical precipitation, microemulsion, sol–gel and hydrothermal crystallization have been developed.[5–11]

Hydrothermal processing is a well-established low-temperature technique to obtain fine powders. The recent innovation in combining the hydrothermal method with a microwave field (M–H) has led to several advantages such as a very rapid heating temperature of treatment and faster kinetics of crystallization with respect to the conventional process (C–H).[12–14] Authors have recently reported the comparison between nanostructured titania (TiO_2) powders synthesized via conventional and microwave hydrothermal methods by forced hydrolysis of $TiOCl_2$.[15] The microwave effects led to spherical nanopowders with a high degree of crystallization in shorter times with respect to the C–H method. In particular, even if the TiO_2 crystals obtained with M–H process are finer than those conventionally synthesized, they are however agglomerated. The performance of titania can be optimized by preventing agglomeration with specific microstructural and macrostructural control over the physicochemical properties of the material. This can be generally attained by both post-synthesis modification, when an organic group is grafted onto the preformed particles or clusters, and by *in situ* functionalization when an organic group is introduced during the synthesis,[16] as in the case of slurry preparation for tape casting production.

Actually, environmental and health aspects of the tape casting process have received special attention leading to the change in the slurry formulations from organic solvent to water.[17] These water-based slurry formulations require the addition of a polymeric dispersant, which increases the electrostatic/electrosteric repulsive forces and consequently eliminates aggregation. Hydroxypropylcellulose (HPC) has been indicated[18] in several studies as an effective compound in suppressing the aggregation of titania particles. Jean and Ring showed that hydroxypropylcellulose provide steric stabilization during the precipitation of titania from alcohol solution, resulting in an uniform particle with lower sensitivity to reaction condition.[19,20] As a matter of

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* Corresponding authors. Fax: +39 0592056243.
E-mail addresses: annamaria.ferrari@unimore.it (A.M. Ferrari), marcello.romagnoli@unimore.it (M. Romagnoli).

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fact such a polymer is adsorbed onto the surface of the particles through hydrogen bonding and creates a steric barrier leading to a repulsive force.

In the present paper, we describe the effect of HPC addition to the TiO_2 nanoparticles aqueous suspensions prepared either with conventional hydrothermal (C–H) or with microwave-assisted hydrothermal (M–H) methods. In order to better evaluate the influence of the polymer dispersant, we selected, on the basis of a previous study,[15] the synthesis conditions which enable to obtain, for both the processing methods, nanopowders with analogous chemical–physical characteristics. As a difference from *in situ* functionalization, where the steric dispersant is used during the production stage, all experiments have been conducted *ex situ* by adding HPC to the titania nanoparticles aqueous suspensions. In fact, the high temperature, pressure and the low pH values used in C–H and M–H hydrothermal synthesis could induce HPC degradation during the synthesis step. The effect of: mixing time between the components of the suspension; HPC and TiO_2 concentration on shear stress of the suspensions have been considered while all the other parameters influencing the rheological behaviour have been kept constant. In order to evaluate their effects and interactions, a design of experiment (DOE) approach has been carried out.[21,22] Differently from the most used methodology as “Trial and Error” or “One Factor At Time”, this statistical procedure can be used to study the mutual influences of two or more independent parameters. DOE is a structured and organized method for determining the relationship between the components and the output of a process. A correct experimental planning permits to get more information with a lower effort and reduces the subjectivity of the results increasing their technical and scientific values. DOE generates a map of the response over a specified region of independent parameters, so it is possible to discover the critical variables, to define mathematical models and, by them, to optimise the product and the process.[23]

DOE is not very used in literature in spite of its efficiency in the study of complex systems where more variables act simultaneously and in few works has been applied to rheological studies.[24,25]

2. Experimental procedure

2.1. Samples preparation

TiO_2 synthesis has been conducted in hydrothermal condition starting from a 0.5 M solution of $TiOCl_2$ with the employment of both a conventional and a microwave thermal treatment in agreement with the procedure described elsewhere.[15]

At first, several experiments have been carried out to determine the optimum conditions for the two investigated processes in order to obtain titania nanoparticles with similar mineralogical composition. On the basis of the results, microwave hydrothermal synthesis has been conducted using a 2.45 GHz microwave digestion system (Model MDS-200, CEM, NC) at 160 °C for 5 min, while the conventional hydrothermal process has been performed at the same temperature for 2 h.

The obtained nanoparticles have been washed several times with double-distilled water to adjust the pH at neutral conditions and successively treated with ethanol to reduce hard aggregation.[26] Titania powders were then redispersed with aqueous solution of HPC (molecular weight 100,000, Aldrich). The concentration of HPC was varied from 0.5 to 1 wt.% with respect to the total suspension weight. Inorganic solid content is 45 and 60 wt.%. The obtained suspensions have been stirred in a fast ball mill for 2 and 20 min in order to perform the rheological measurements. These ranges have been fixed considering possible industrial applications, in particular textile coatings. While low HPC values and short mixing time have been used for economic reasons, the amount of solid has been chosen equal or lower than 60 wt.% in order to prepare suspensions with a viscosity not excessively high to be applied.

2.2. Samples characterization

The synthesized titania nanoparticles have been analysed with a computer-assisted conventional Bragg–Brentano diffractometer using the Ni-filtered Cu Kα monochromatic radiation ($\lambda = 1.5418$ Å) (PW3710 Philips). The X-ray diffraction (XRD) patterns have been collected at room temperature in a 2θ range of 20–80°, with a scanning rate of $0.005^\circ\ s^{-1}$ and a step size of 0.02°. The quantitative analysis of the obtained samples has been performed by the combined Rietveld–R.I.R. (reference intensity ratio) method. A 10 wt.% of corundum (NIST SRM 674a annealed at 1500 °C for 1 d to increase the crystallinity to 100 wt.%) has been added to all samples as internal standard. The mixtures, ground in an agate mortar, have been side-loaded in an aluminium flat holder in order to minimize the preferred orientation problems. Data have been recorded in the 5–140° 2θ range (step size 0.02° and 6 s counting time for each step). The phase fractions extracted by the Rietveld–R.I.R. refinements, using GSAS and EXPGUI,[27,28] have been rescaled on the basis of the absolute weight of corundum originally added to the mixtures as an internal standard, and therefore internally renormalized.

Sample morphology has been examined by transmission electron microscopy (TEM, JEM 2010, JEOL). For TEM observation, specimens have been prepared by dispersing the as-obtained powders in distilled water and than placing a drop of suspension on a copper grid with a transparent polymer followed by drying.

Suspensions shear stress values have been measured with a Haake RS100 control stress rheometer, using a plate-cone sensor system, where the cone has a diameter of 20 mm and 1° of angle. This study has been conducted by applying a *factorial design* statistical experimental method,[22] with which informations on the optimal operational parameters for producing aqueous suspensions of monodispersed nanosized titania particles have been obtained. Concerning the independent parameters: mixing time; shear rate; solid and HPC content have been considered. The run order for experiments has been randomised to counteract any time-related effects. Least squares method and ANOVA analysis have been used to define a mathematical model (Design-Expert v. 7.0.3 by Statease), statistically valid, able to describe the relationship between the independent variables and shear

Table 1
Composition of the suspensions measured

Nr.	Solid (%)	Mixing time (min)	HPC (%)
1	45.00	2.00	0.50
2	60.00	2.00	0.50
3	45.00	20.00	0.50
4	60.00	20.00	0.50
5	45.00	2.00	1.00
6	60.00	2.00	1.00
7	45.00	20.00	1.00
8	60.00	20.00	1.00

stresses measured. The values of the parameters are reported in Table 1.

3. Results and discussion

XRD patterns of microwave and conventional hydrothermally synthesized TiO_2 nanopowders, obtained at 160 °C for 5 and 120 min, respectively, are shown in Fig. 1.

From the XRD, it can be seen that all titania samples are mainly composed of the rutile phase with a minor amount of anatase, independently on the synthesis method used. Furthermore, a smaller peak broadening can be observed in C–H nanopowders being dependent on the longer reaction time with respect to the M–H route.

The quantitative analysis of the powders has been performed in order to verify if the two processing methods have the same influence on both the crystallinity and the composition of the samples (see Fig. 2 as an example). The results of the Rietveld–R.I.R. refinements, summarized in Table 2, show how the synthesized nanopowders have the same mineralogical composition independently on the synthesis method used.

The morphology of the as-prepared titania powders observed by TEM analysis is shown in Fig. 3. In all cases the TiO_2 particles are aggregated into clusters in the range of several hundred nanometers. The analysis shows that primary nanocrystals obtained under C–H conditions are constituted of many spherical crystals of pure rutile phase (average dimension 30 nm) and some rod-like shaped particles of anatase phase (80 nm × 20 nm) connected tightly to one another. Rutile is again the dominant crystallized phase in the M–H titania nanopowders (10 nm) with small amount of anatase (40 nm × 10 nm), but the lower particle size with respect to the conventional ones suggest an extremely rapid crystallization due to the generation of localized high temperatures in the microwave field.

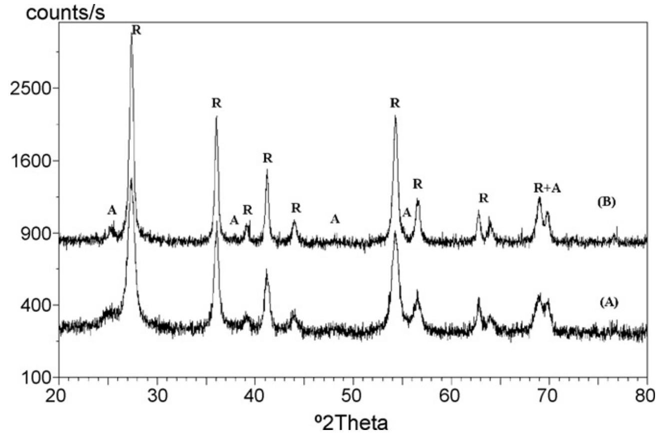

Fig. 1. X-ray diffraction spectra of (A) M–H and (B) C–H hydrothermally synthesized nanopowders.

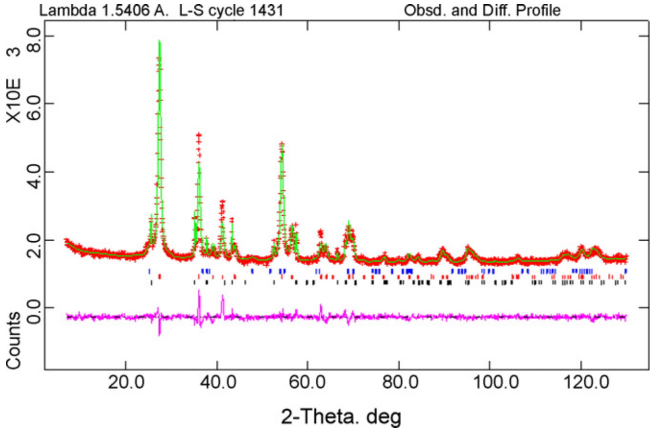

Fig. 2. Observed (crosses), calculated (continuous line) and difference curve from the Rietveld–R.I.R. refinement of the M–H sample. Markers representing the phase reflections correspond to corundum, rutile and anatase (from bottom to top).

The statistical treatment of the rheological measurements has enabled the elaboration of mathematical models and permitted not only to simulate the suspensions behaviour, but also to evaluate the contribution of the various experimental parameters involved in. The DOE study of the suspension rheology has been carried out by measuring shear stress at five, equally spaced, different shear rates ranging from 50 to 250 s^{-1}. The choice of these shear rates is due to the industrial textile applications where the suspension have to be applied. The samples showed flow curves with a non-Newtonian behaviour. It was verified fitting the data with the Herschel–Bulkley law (Eq. (1))

$$\sigma = \sigma_o + K\dot{\gamma}^{n} \tag{1}$$

where σ is the shear stress (Pa), σ_o the yield stress (Pa), K the consistency (Pa s^{-1}), $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the power law exponent.

The n parameters calculated for the samples are resulted both lower (shear thinning) and higher (shear thickening) than one,[29] due to the different parameters of preparation, confirming the non-Newtonian behaviour of the suspensions.

Table 2
Phase composition (%) and standard Rietveld-R.I.R. agreement factors obtained for the C–H and M–H samples

Phases %	CH 160 °C, 120 min	MH 160 °C, 5 min
Rutile	77.9 (2)	79.5 (1)
Anatase	5.9 (1)	5.1 (1)
Amorphous	16.1 (1)	15.3 (1)
Total	99.9	99.9
χ^2	2.96	2.33
Rwp	0.043	0.038
Rp	0.031	0.027

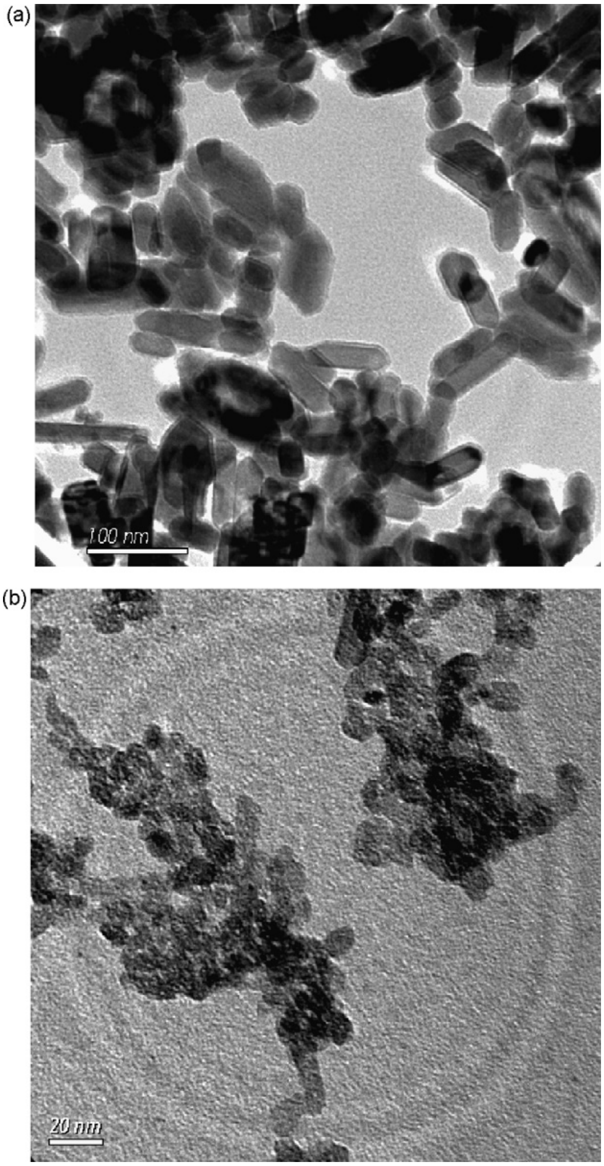

Fig. 3. TEM micrographs of (a) C–H and (b) M–H titania nanopowders.

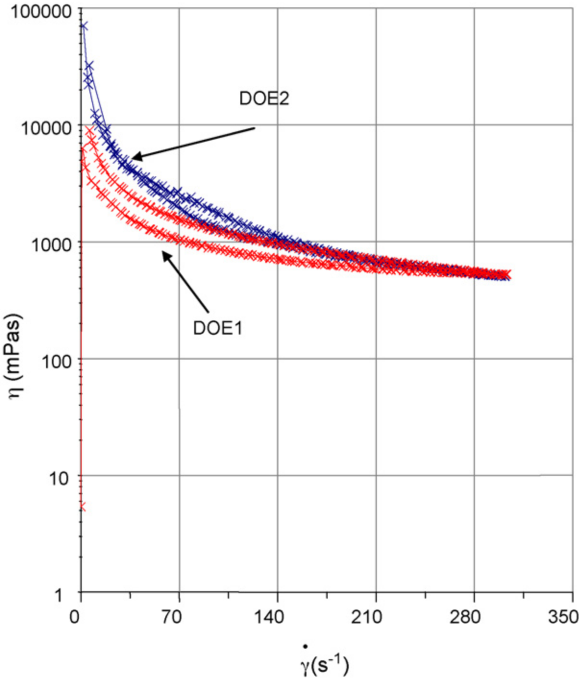

Fig. 4. Apparent viscosity versus shear rate for two different compositions corresponding to a solid content of 60 wt.%.

A hysteresis between the up and down curves is evident in some samples. It could be a signal of thixotropy that has to be deeper investigated with further analysis. In Fig. 4, the graphs of apparent viscosity versus shear rate for compositions 1 and 2 of Table 1 are reported as representative.

By ANOVA analysis, the coefficients with statistical relevance have been defined, while by least squares method their coefficients in the mathematical model have been calculated. A base 10 log transformation has been necessary to fit better the measured data. The result of the analysis is the following equation:

$$\mathrm{Log}\sigma = -4.88 + 0.10S - 0.07T + 6.23H + 0.01\dot{\gamma} + 2.77 \times 10^{-3}ST - 0.10SH - 2.33 \times 10^{-4}T\dot{\gamma} - 8.87 \times 10^{-3}H\dot{\gamma} \qquad (2)$$

where σ is the shear stress (in mPa), S the solid content (wt.%), T the mixing time (min), H the amount of HPC (wt.%) and $\dot{\gamma}$ is the shear rate (s^{-1}).

The agreement between calculated shear stress values obtained with Eq. (2) with respect to the measured ones is very high, being the coefficient of correlation for 28 points $R^2 = 0.9408$. However, it is necessary to remind that the model has its validity only within the range of the independent variables used.

3.1. Main effects

The solid content has a positive coefficient in Eq. (2). It means that, when it increases, both the shear stress and the viscosity increase as well. Such effect has been widely examined and it is well known.[30,31] It can be explained with the fact that the number of impacts among the particles increases with the increasing of the number of particles in suspension. The phenomenon determines energy dissipation that, at macroscopic scale, increases the shear stress and the apparent viscosity. Solid content interacts with other parameters, but the final influence remains the same of the main effect.

On the contrary, the mixing time shows a negative coefficient. It means that the parameter acts to decrease the shear stress. It likely improves the dispersion grade of the solid in the suspension avoiding the formation of TiO_2 aggregates. However, it is also involved in interaction terms with other parameters such as shear rate and solid percentage. Its influence on the system is therefore more complex and better described in the next paragraphs.

HPC addition has a positive coefficient because the shear stress increases as the HPC content is also increased. This

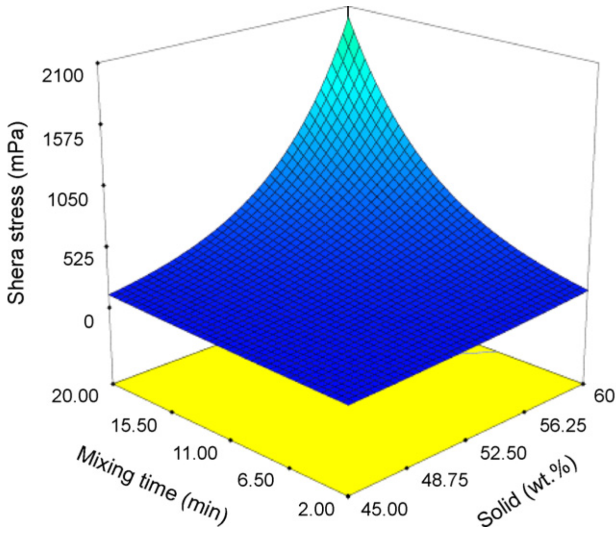

Fig. 5. 3D surface response of shear stress versus solid content and mixing time. $\dot{\gamma} = 150\,\mathrm{s}^{-1}$; HPC = 0.75%.

behaviour is unexpected, but could be explained considering the flocculation effect of the deflocculant when it is added in an excessive amount (over-deflocculation). This phenomenon can be also observed when HPC is added to water alone: the system increases its viscosity according to the percentage of the organic substance used. Finally, it is important to remark that HPC percentage is involved, as mixing time, in interactions with solid content and shear rate so its global effect must be evaluated considering also the influence of the other parameters.

Finally, the shear rate coefficient has found to be positive in agreement with other rheological studies on ceramic suspensions, but binary interactions are, also in this case, statistically significant and, consequently, the global effect is slightly complex.

Comparing these main effects and considering their relative magnitudes, solid content is the most important parameter.

3.2. *Interaction among the parameters*

All the analysed parameters show mutual binary interactions. The 3D surface plot of σ versus the solid content and the mixing time is shown in Fig. 5. HPC and shear rates are kept constant at, respectively, 0.75 wt.% and $150\,\mathrm{s}^{-1}$. The response is represented by a surface that strongly increases when mixing time and solid also increase, even if they have opposite coefficients when individually considered. This behaviour is less evident at the lowest solid content due to the low viscosity of the suspension. The occurrence that mixing time increases the shear stress only when associated with the solid content is less expected. In fact, it should improve particles dispersion with a consequent reduction of shear stress or, at least, a lower increase rate. Even if the mixing time main coefficient in Eq. (2) is negative, the global result is the product of the sum of two synergic effects: with the solid content (coefficient in Eq. (2) equal to $+2.77 \times 10^{-3}$) and with the shear rate (coefficient in Eq. (2) equal to -2.33×10^{-4}). Low mixing time seems to reduce the effect on shear stress due to the increasing of solid content. Even though in this work such phenomenon has not been deeply discussed because it is not the main purpose of this paper, the inclusion of air in the suspension during the mixing step is the main suspected of this behaviour. Air bubbles could act as an additional phase that, even if different with respect to TiO_2, however contribute to increase the shear stress and the viscosity as well. They could be considered equivalent to soft particles deformed or broken at higher shear rates. In Fig. 6, shear rate and mixing time versus shear stress is presented. As expected, at low mixing time, σ increases with $\dot{\gamma}$ while, at high mixing time, the trend is reversed or the shear stress almost does not change when shear rate increases. Considering the previous hypothesis, if the mixing time produces air bubbles inside the suspension, when $\dot{\gamma}$ increases, bubbles could be broken with the consequent reduction of σ. Obviously, at high mixing time, when the concentration of bubbles is high, the effect appears more evident.

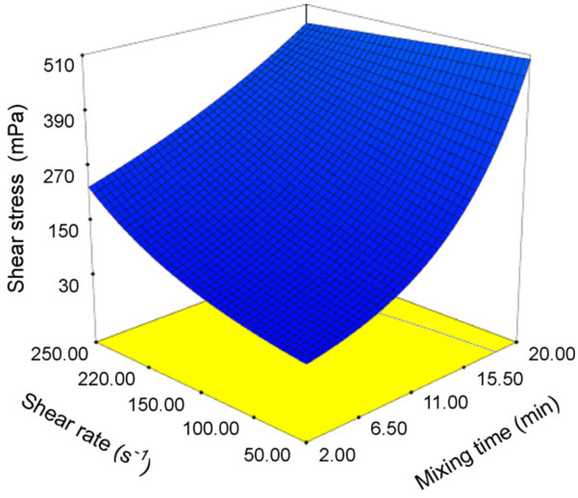

Fig. 6. 3D response surface for shear stress versus shear rate and mixing time. Solid content = 52.50 wt.%; HPC = 0.75%.

The deflocculant effect of HPC and mixing time on shear stress is shown in Fig. 7. This behaviour is well known in rheology science of suspensions: the organic additive reduces shear stress and viscosity. Moreover, HPC reduces the effect of mixing time on the shear stress and, consequently, on the viscosity, especially at the higher solid content. This result can be explained considering that HPC reduces the inclusion of air in the suspension by lowering its viscosity. In fact, at low viscosity, bubbles are able to get to the surface and to leave it faster than when the viscosity is high. As explained above, the concentration of bubbles affects the shear stress value. Passing from low to high percentage of TiO_2, a change of σ surface is observed. At low solid content, when HPC increases, the shear stress shows an increment below $180\,\mathrm{s}^{-1}$ while, at medium and high solid content, HPC reduces the shear stress. This effect can be related to the fact that HPC is added in percentage with respect to the total weight of the suspension. To a given percentage, when the concentration of TiO_2 is at its lower values, the effective HPC concentration on the particle surface is probably higher than when the solid content is medium or high. Considering the well

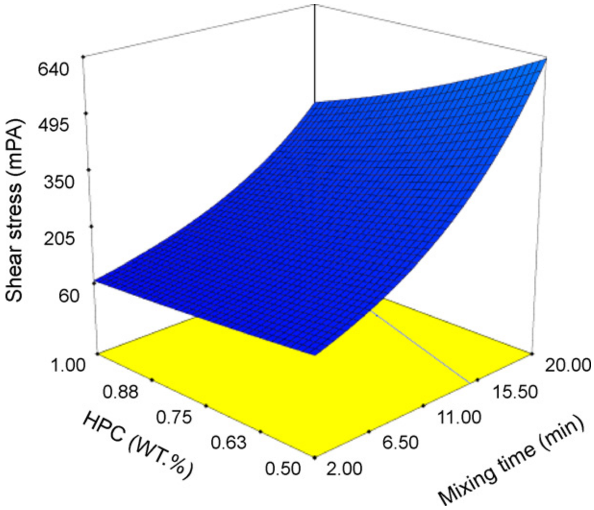

Fig. 7. The effect of mixing time and HPC wt.% on shear stress $\sigma \cdot \dot{\gamma} = 150\,\mathrm{s}^{-1}$; solid content = 52.50 wt.%.

known effect of over-deflocculation, the optimal concentration of HPC decreases when the solid content also decreases and vice versa. Over 180 s^{-1}, the shape of the shear stress surface changes its slope, but the reasons are not clear and further studies have to be pursued.

HPC contributes to reduce the shear stress growth rate when shear rate increases, as shown in Fig. 8. From a qualitatively point of view, the surface shape does not significantly change with the variation of solid percentage and mixing time even if the shear stress increases as the solid is increased and vice versa. Also in this case the mixing time shows a pejorative effect on the shear stress.

The analysis using DOE has highlighted the importance of interactions on the final effect of the parameters. In general, interactions are less important than main parameters, but in some cases their influence is so important to change significantly the analysis of the system. In particular, the mixing time is strongly affected by interaction with the other parameters that overturns the main effect.

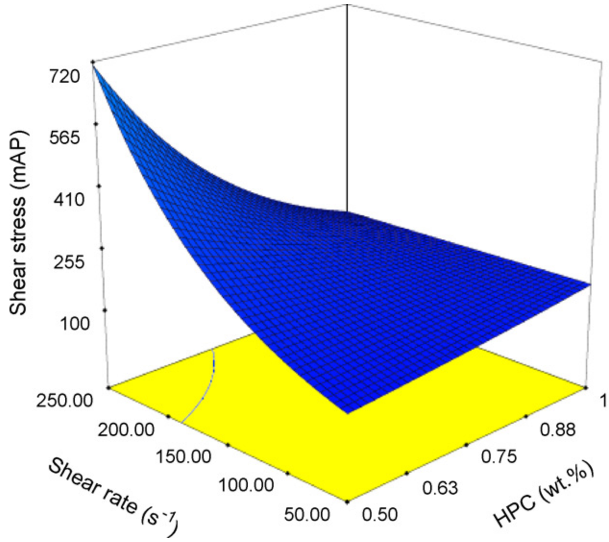

Fig. 8. Effect of shear rate and HPC% on shear stress σ. Solid content = 52.50 wt.%; mixing time = 11 min.

4. Conclusions

The DOE approach has proved to be an efficient method to study the rheology of nanoparticle suspension. Mathematical models can be used to predict and better analyse its behaviour in different condition with a limited number of experimental tests. In this study, the obtained model has confirmed the effect of solid content; HPC percentage and shear rate on shear stress while it has highlighted the effect of mixing time as growth factor of shear stress. The agreement between calculated shear stress values with respect to the measured ones is very high for all the samples and shear rates.

A synergic interaction has been observed between mixing time and solid content on the increasing of shear stress. The effect is probably due to the inclusion of air in the suspension during the mixing step. The HPC confirm its deflocculant effect on the suspension. Moreover, it reduces the effect of mixing time on the shear stress and, consequently, on the viscosity, especially at the higher solid content.

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References

1. Zheng, Y., Shi, E., Chen, Z., Li, W. and Hu, X., Influence of solution concentration on the hydrothermal preparation of titania crystallites. *J. Mater. Chem.*, 2001, **11**(5), 1547–1551.
2. Ferroni, M., Guidi, V., Martinelli, G., Faglia, G., Nelli, P. and Sberveglieri, G., Characterization of a nanosized TiO_2 gas sensor. *Nanostruct. Mater.*, 1996, **7**(7), 709–718.
3. Blake, D. M., Webb, J., Turchi, C. and Magrini, K., Kinetic and mechanistic overview of titania-photocatalyzed oxidation reactions in aqueous solution. *Solar Energy Mater.*, 1991, **24**(1–4), 584–593.
4. Karch, J., Birriger, R. and Gleiter, H., Ceramics ductile at low temperature. *Nature*, 1987, **330**(10), 556–558.
5. Scolan, A., Sanchez, C. and Synthesis, Characterization of surface-protected nanocrystalline titania particles. *Chem. Mater.*, 1998, **10**(10), 3217–3223.
6. Stathatos, E., Lianos, P., Del Monte, F., Levy, D. and Tsiourvas, D., Formation of TiO_2 nanoparticles in reverse micelles and their deposition as thin films on glass substrates. *Langmuir*, 1997, **13**(16), 4295–4300.
7. Chhabra, V., Pillai, V., Mishra, B. K., Morrone, A. and Shah, D. O., Synthesis, characterization, and properties of microemulsion-mediated nanophase tio_2 particles. *Langmuir*, 1995, **11**(9), 3307–3311.
8. Zhou, X. F., Chu, D. B., Wang, S. W., Lin, C. J. and Tian, Z. Q., New route to prepare nanocrystalline TiO_2 and its reaction mechanism. *Mater. Res. Bull.*, 2002, **37**(11), 1851–1857.
9. Wang, C. and Ying, J. Y., Sol–gel synthesis and hydrothermal processing of anatase and rutile titania nanocrystals. *Chem. Mater.*, 1999, **11**(11), 3113–3120.
10. Aruna, S. T., Tirosh, S. and Zaban, A., Nanosize rutile titania particle synthesis via a hydrothermal method without mineralizers. *J. Mater. Chem.*, 2000, **10**(10), 2388–2391.
11. Wu, M., Lin, G., Chen, D., Wang, G., He, D., Feng, S. *et al.*, Sol–hydrothermal synthesis and hydrothermally structural evolution

of nanocrystal titanium dioxide. *Chem. Mater.*, 2002, **14**(5), 1974–1980.

12. Komarneni, S., Rajha, R. K. and Katsuki, H., Microwave–hydrothermal synthesis of ceramic powders. *Mater. Res. Bull.*, 1992, **27**(12), 1393–1405.
13. Komarneni, S. *et al.*, Microwave–hydrothermal processing of titanium dioxide. *Mater. Chem. Phys.*, 1999, **61**, 50–54.
14. Bondioli, F., Ferrari, A. M., Leonelli, C., Siligardi, C. and Pellacani, G. C., Microwave–hydrothermal synthesis of nanocrystalline zirconia powders. *J. Am. Ceram. Soc.*, 2001, **84**(11), 2728–2730.
15. Corradi, A. B., Bondioli, F., Focher, B., Ferrari, A. M., Grippo, C., Mariani, E. *et al.*, Conventional and microwave–hydrothermal synthesis of TiO_2 nanopowders. *J. Am. Ceram. Soc.*, 2005, **88**(9), 2639–2641.
16. Kubo, M., Kasahara, T., Takeda, H. and Yonemoto, T., Synthesis of monodispersed nanosize titania particles by alkoxide method in the presence of hydroxypropylcellulose. *J. Chem. Eng. Japan*, 2004, **37**(6), 785–790.
17. Hotza, D. and Greilb, P., Aqueous tape casting of ceramic powders. *Mater. Sci. Eng.*, 1995, **A202**, 206–217.
18. Bessekhouad, Y., Robert, D. and Weber, J. V., Synthesis of photocatalytic TiO_2 nanoparticles: optimization of the preparation conditions. *J. Photochem. Photobiol. A: Chem.*, 2003, **6286**, 1–7.
19. Jean, H. and Ring, T. A., Effect of a sterically stabilizing surfactant on the nucleation, growth and agglomeration of monosized ceramic powders. *Colloid Surf.*, 1988, **29**, 273–291.
20. Jean, H. and Ring, T. A., Processing monosized TiO_2 powders generated with HPC dispersant. *Am. Ceram. Soc. Bull.*, 1986, **65**(12), 1574–1577.
21. Full factorial designs. http://www.itl.nist.gov/div898/handbook/pri/section3/pri333.htm.
22. Montgomery, D. C., *Design and Analysis of Experiments* (*5th ed.*). John Wiley & Sons, 2000, p. 478–490.
23. Bondioli, F., Ferrari, A. M. and Romagnoli, M., Effect of sintering condition on linear shrinkage of porcelainized stoneware tiles by two full factorial experimental design. *Tile Brick, Manual*, 2006, 18–21.
24. Gomes, C. M., De Noni Jr., A., Reis, J. P., Oliveira, A. P. N. and Hotza, D., Using mixture design to optimize the amount of deflocculant in triaxial ceramic suspensions. *Am. Ceram. Soc. Bull.*, 2004, **11**, 9301–9304.
25. Romagnoli, M. and Andreola, F., Mixture of deflocculants: a systematic approach. *J. Eur. Ceram. Soc.*, 2006, **27**(2–3), 1871–1874.
26. Mayo, M. J., Seidensticker, J. R., Hague, D. C. and Carim, A. H., Surface chemistry effects on the processing and superplastic properties of non-crystalline oxide ceramic. *Nanostruct. Mater.*, 1999, **11**(2), 271–282.
27. Larson, A. C. and Von Dreele, R. B., *General structure analysis system* (*GSAS*). Los Alamos National Laboratory Report LAUR; 2000, p. 86–748.
28. Toby, B. H., *EXPGUI*, a graphical user interface for *GSAS*. *J. Appl. Cryst.*, 2001, **34**, 210–213.
29. Romagnoli, M. In: SALA editor. *Technical Glossary in Rheology Applied to Ceramics*. Italian Ceramic Society I.Cer.S; 2006, p. 409.
30. Barnes, H. A., Hutton, J. F. and Walters, K., In *An Introduction to Rheology*. 5th ed. Elsevier Science, 2001. p. 119–120, ISBN: 0444871403.
31. Barnes, H. A., *A Handbook of Elementary Rheology*. University of Wales, Institute of Non-Newtonian Fluid Mechanics, 2000, p. 122–126.