Ultrasonic Treatment Enhanced Surface Modification of Titanium Oxide by Tailor-Made Surface-Active Polymers

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Abstract

The surface modification of titanium dioxide in aqueous dispersions of specially tailor-made periodic acrylic acid/isobutylene copolymers, poly(acrylic acid)/polystyrene graft copolymers, and hydrophobically modified polyethyleneoxide urethane (HEUR) by ultrasonic treatment was studied. The pigment surface modification by the above copolymers was comparatively investigated regarding conventional adsorption as contrasted to an ultrasonic treatment assisted procedure. The course and efficiency of the polymer adsorption onto the pigment surface was quantified by electrokinetic sonic amplitude measurements. The higher efficiency of the pigment surface coating by the copolymers as achieved by ultrasonic treatment varies with the copolymer architecture and is a consequence of ultrasonically induced pigment surface activation.

Introduction

The homogeneous dispersing of pigments is important in coatings formulations. For producing aqueous pigment dispersions, many approaches have been described in literature [1 - 3]. It was shown [4 - 6] that highly stable dispersions are obtained by ultrasonic treatment of pigment slurries in aqueous solutions of polymer surfactants. Recent studies [7, 8] by employing electrokinetic sonic amplitude (ESA) measurements have revealed that the origin of the improved stabilization of the pigment dispersion is due to first the generation of a finer dispersion of the pigment by the mechanical, *i.e.*, ultrasonic treatment, and second the formation of a thicker layer of the polymeric additive around the pigment; the better encapsulation of the pigment by the stabilizer polymer is a consequence of the ultrasonically induced activation of the pigment surface.

In this work, we report on the dispersing of TiO_2 in aqueous solutions of amphipolar copolymers of well-defined structures by ultrasonic treatment. These copolymers are characterized by special sequences of hydrophilic and hydrophobic units which result in specific pigment-polymer interactions and stabilizing properties [9 - 11]. The effect of the ultrasonic treatment on the deposition of the stabilizer copolymer is discussed in the context of the various copolymer architectures.

Experimental

Materials

Titanium dioxide rutil pigment Kronos 2310 with particle size 0,3 μm was used as received. The synthesis and properties of the acrylic acid (AA) containing AA/isobutylene (IB) copolymers P([IB-AA]-r-AA) and methacrylic acid (MAA)/styrene (S) graft copolymers as well as the synthesis of the hydrophobically modified poly(ethylene oxide) urethanes (HEUR) have been described elsewhere [9, 10, 12, 13]. The total AA content of the P([IB-AA]-r-AA) copolymers varied between 55 and 100 mol.%, and the molecular weight was $46.000 \leq Mn \leq 64.000$ [9, 10]. The PMAA-g-PS graft copolymer consists of a PMMA backbone of Mn = 2.600 and in average 1,8 PS-grafts of Mn = 1.300 [10].

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Techniques

For the preparation and investigation of the TiO_2 pigment dispersions, amphipolar copolymers were predissolved in water, and then the powdery pigment was added. After premixing with a laboratory stirrer (700 rpm for 10 min), the system was treated with ultrasound for 2 min with an ultrasonic generator Branson Sonifier B-12 with actual power of $1,5 \text{ W/cm}^2$.

The pigment-copolymer interaction and the formation of the polymeric adsorption layer were investigated by ESA measurements as described earlier [7,11]. The particle size was measured by both ESA and by using a Malvern Instruments Nanosizer [7]. Instrumental uncertainties have not exceeded 1%. For sedimentation measurements, the obtained dispersions were poured into test-tubes and the sedimentation kinetics were monitored by following the border line between the turbid and the transparent zones; the refraction index of the supernatant liquid was measured by standard optical devices.

Results and discussion

Acrylic acid (AA) based periodic copolymers P([IB-AA]-r-AA) consisting of alternating isobutylene (IB) – AA sequences [IB-AA]m interrupted by (AA)n sequences, and graft copolymers PMAA-g-PS consisting of poly(methacrylic acid) (PMAA) backbone and polystyrene (PS) grafts of various structure were already shown to act as stabilizers of TiO_2 aqueous dispersions [9, 10]. In these studies the dispersions had been prepared by conventional stirring, and then the pigment-polymer interaction and their stability were measured.

TiO₂ - (IB-AA-r-AA) System

As already mentioned above, the acrylic acid (AA)/isobutylene (IB) copolymer consists of sequences of alternating AA-IB units and homosequences of AA as illustrated in the chemical formula 1:
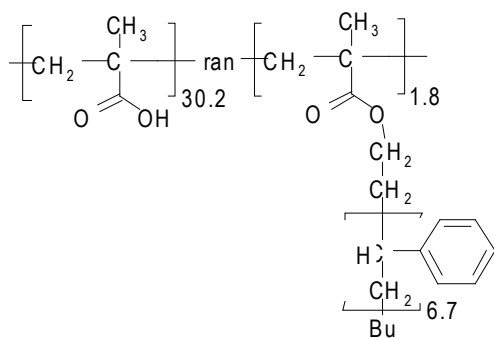
The alternating AA-IB sequence is relatively hydrophobic as compared to the strongly hydrophilic (AA)n homosequence. Earlier studies of the copolymer-pigment interaction by means of the ESA method had revealed that the saturation concentration SC increases with decreasing AA content and that the (AA)n homosequences act as anchor to the pigment, and electrosteric stabilization is predominantly achieved through loops of alternating AA-IB sequences [9, 10].

The effect of ultrasonic treatment on the copolymer-pigment interactions has been investigated exemplarily for the water soluble copolymer (P(IB-AA-r-AA)-1) containing 82 mole-% AA comonomer which in earlier work [9] was shown to be one of the most effective dispersion stabilizing copolymer of this series. The comparative ESA measurements of the aqueous dispersion of TiO_2 (without as well as with different amounts of added copolymer as stabilizer) for systems without and with ultrasonic treatment can give quantitative information about the process of polymer adsorption. This is reflected first from the dependence of the dynamic mobility μ on the relative polymer concentration [11] as shown in Fig. 1, and second from the comparison of this dependency for the system without and with ultrasonic treatment (Fig. 1, curves 1 and 2).

The increase in the dynamic mobility with increasing polymer concentration (relative to the TiO_2 concentration) reflects the increase of the zeta potential, and the reaching of a plateau means that an adsorption equilibrium has been reached (see Fig. 1, curve 1). This is primarily a consequence of the complete occupation of positively charged sites on the TiO_2 surface by negatively charged carboxylate groups of the (AA)n homosequences; the high number of ionizable carboxylic groups in the alternating IB-AA sequence loops of the adsorbed copolymer are responsible for an increased charge density of the copolymer coated pigment as compared to the pure TiO_2 pigment. The same observation holds true for the ultrasonically treated system (Fig. 1, curve 2).

The comparison of the dynamic mobility vs. copolymer concentration curves of the ultrasonically treated system with the untreated system (Fig. 1) reveals the distinct effect of ultrasonic treatment similarly as already observed for other systems [7, 8]. Without ultrasonic action, the formation of a polymeric adsorption layer on the pigment surface seems to be approached already below a polymer concentration of about 0,5 wt.-% whereas this is only the case for a polymer concentration of about 2 wt.-%

when ultrasonification was applied. The polymer concentration (relative to TiO$_2$ mass) are also referred to as the so-called saturation concentration SC which is defined as the polymer concentration above which the dynamic mobility does only little increase [11]; SC is approximately 0,3 wt.-% [9, 10] and is given by the intercept of the tangents to the initial sharp increase and to the approaching of the plateau (see Fig. 1).
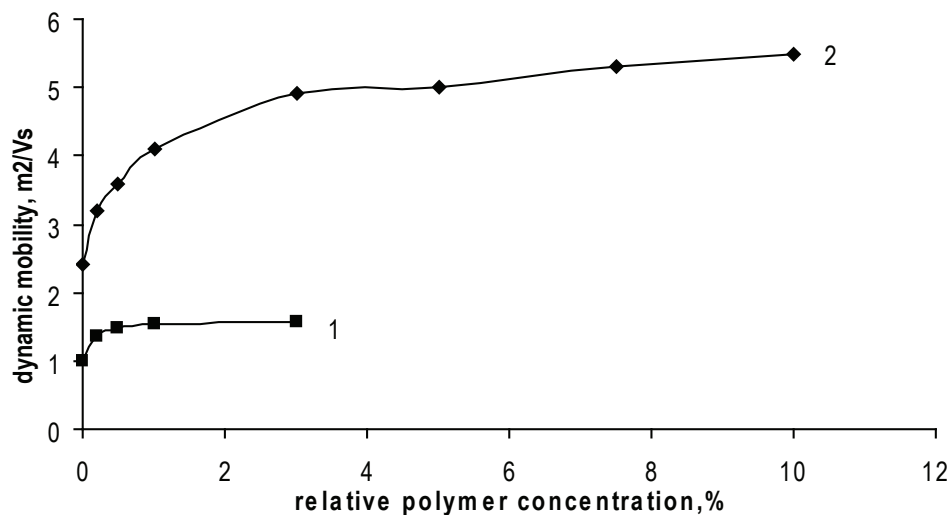

Fig. 1. Dependence of the dynamic mobility on the relative concentration of P([IB-AA]-r-AA)-1 (82 % AA) for 1 % TiO$_2$ aqueous dispersion with (♦) and without (■) ultrasonic treatment.

In this context it must be emphasized that the initial dynamic mobility of the pristine TiO$_2$ is already much higher in the presence of ultrasonic action (Fig. 1, curve 2) which illustrates the already initially higher zeta potential as compared to the untreated system. A common feature of both the ultrasonically treated and untreated system is that further addition of polymer beyond the SC does not appreciably change the dynamic mobility meaning that polymolecular adsorption doesn't appear to occur.

The effect of ultrasonic treatment on the colloidal stability of the aqueous TiO$_2$ dispersions, stabilized by the IB/AA copolymers of different monomer sequence periodicity, is given in Tab. 1.

Table 1.
Sedimentation stability of TiO$_2$ aqueous dispersions stabilized by IB/AA copolymers of number average molecular weight Mn and given total AA content

Copolymer	Mn	mole % of AA	Suspension stability (half-time of the sedimentation, days)	
			Without mechanical action	With mechanical action (ultrasonic treatment)
PAA	200.000	100	8	14
P(IB-AA-r-AA)-1	55.000	82	7	10
P(IB-AA-r-AA)-2	46.000	60	4	3
P(IB-AA-r-AA)-3	56.000	54	6	10
P(IB-AA-r-AA)-4	64.000	52	7	16

First it is evident that, irrespective of the constitution of the copolymer, the ultrasonification substantially improves the dispersion stability as reflected from the comparison of the sedimentation half times of the non-treated and treated systems. The data also infer that there is an optimal copolymer structure with regard to the mole fraction of alternating IB-AA sequences and AA homosequences (P(IB-AA-r-AA)-4)); this is in accordance with previously discussed constitutional effects [9].

TiO₂ – PMAA-g-PS System

The effect of the ultrasonification on the adsorption of the amphipolar graft copolymers PMAA-g-PS consisting of poly(methacrylic acid) (PMAA) backbone and polystyrene (PS) grafts
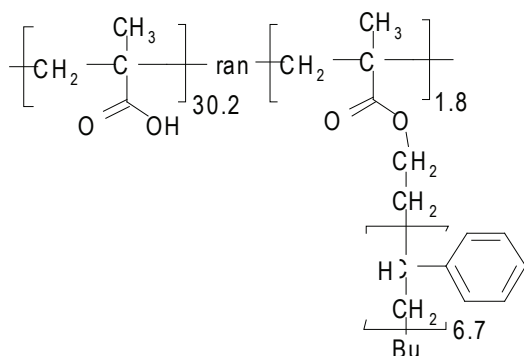

onto TiO₂ is phenomenologically similar as observed for the IB/AA copolymers: the change in the

dynamic mobility is much more pronounced for the ultrasonically treated dispersion than for the non-treated system (see Fig. 2).

The mechanism of the copolymer adsorption via a sequential mono- and bilayer formation followed by the deposition of solloids has already been discussed elsewhere [10]. Again, the adsorption of the graft copolymer ultimately means an increase of the charge density through the carboxylic groups of the PMAA backbone; this is reflected by the increased dynamic mobility, and thus a ξ-potential upon addition of the graft copolymer. If one were to attribute a higher statistical weight to the data point at 0,5 wt.-% in Fig. 2, curve 1, and at 1 wt.-% in Fig. 2, curve 2, respectively, a curve with a shoulder in this concentration range would result; such a curve could be tentatively explained by the transition from the bilayer covered to the solloid covered pigment.

TiO₂ – HEUR System

The addition of the nonionic HEUR consisting of hydrophobic alkyl end blocks and a hydrophilic poly(ethylene oxide) center block,
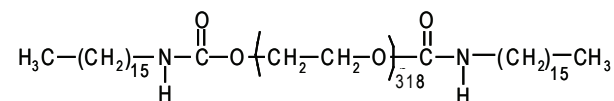
which is usually employed as an associative thickener for aqueous latex dispersion coatings formulations, leads to a decrease of the dynamic mobility
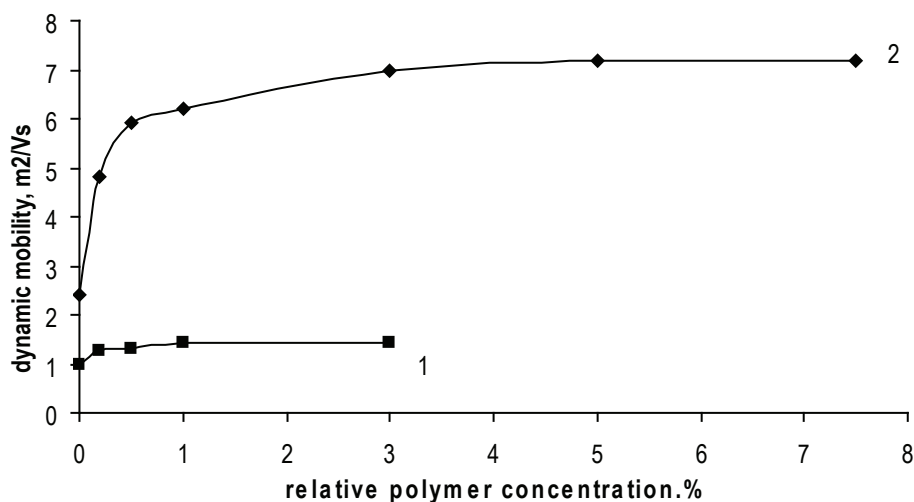

Figю 2. Dependence of the dynamic mobility on the relative concentration of PMAA-g-PS (71 % MAA) for 1 % TiO₂ aqueous dispersion with (♦) and without (■) ultrasonic treatment. The insert is a magnification of curve 1.

of the system when adsorbing on the TiO₂ surface [14]. This is due to the shielding of the charges present on the TiO₂ pigment surface by the hydrophobic hydrocarbon end blocks of the HEUR triblock copolymer.

In comparison to the ionic (M)AA based copolymers discussed above, it is obvious that the adsorption of the non-ionic amphipolar HEUR must result in a decrease of the ξ-potential since no ionic groups are introduced which, as a net result, can overcompensate the shielding of the charged TiO₂ by polymer adsorption (Fig. 3).
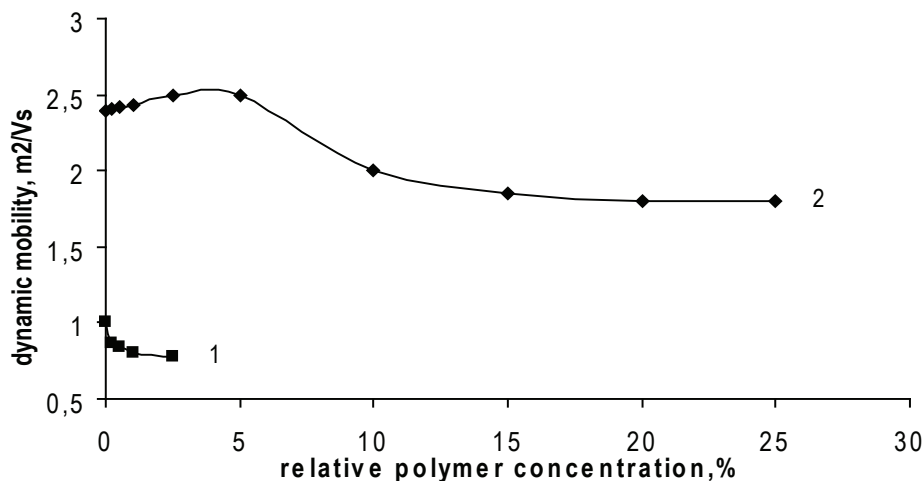

Fig. 2. Dependence of the dynamic mobility on the relative concentration of PMAA-g-PS (71 % MAA) for 1 % TiO₂ aqueous dispersion with (♦) and without (■) ultrasonic treatment. The insert is a magnification of curve 1.

The saturation concentration for the non-treated sample (SC about 0,15 %) is relatively small and in accordance with earlier results [13]. In contrast to this, the saturation concentration is much higher for the ultrasonically treated sample (SC about 12 %). This clearly shows the dual effect of the ultrasonification, *i.e.*, the improvement of the particulate pristine pigment dispersion (which also means an increase of the total pigment surface area) and the simultaneous creation of a highly activated pigment surface.

Correlation of ESA data with the thickness of the coating on the pigment particle

Comparing the values of saturation concentration SC without and after ultrasonic treatment, shows that the amount of polymer adsorbed on the particle surface significantly increases upon ultrasonification. However, as already mentioned above, the decrease of the pristine particle size by the application of the ultrasonic power, and consequently the increased total surface area, automatically leads to an increasing of the amount of polymer deposition.

In order to get some quantitative information about the polymer adsorption as revealed from the ESA data, and to correlate the amount of polymer adsorbed with the dispersing conditions, calculations of the

surface area of the pristine pigment particle and of the polymer coated particle were done for both the systems without and with ultrasonic treatment and related to the amount of adsorbed polymer.

In these calculations a spherical shape of the pigment particle was assumed, and that the maximum polymer adsorption is indicated by the saturation concentration SC; this saturation concentration is reached when the dynamic mobility vs. relative polymer concentration curve (Fig. 1 – 3) becomes more or less parallel to the abscisa and doesn't change much for increasing polymer concentration [13].

First, the total surface area Stot of the particles with surface area Spart is obtained from the measured average particle diameter dpart and the particle number density in the dispersion. Since the saturation concentration SC as obtained by ESA measurements corresponds to the total mass of amphiphilic polymer that is adsorbed on the dispersed particles, the increased particle diameter (due to the adsorbed polymer) and thus the thickness of the polymer adsorption layer can be calculated as well. For the background and the equations on which the calculations of the data compiled in Table 2 are based it is referred to the literature [7].

Table 2

Effect of ultrasonic treatment on the particle diameter dpart, and effect of ultrasonic treatment on the increase
of the particle surface area (Stot) as well as on the saturation concentration (SC) of added amphipolar copolymer
as expressed by the corresponding Stot and SC ratio; the indexes 1 and 2 refer to the non-treated (1) and
ultrasonically treated (2) sample

Amphipolar Copolymer	Averaged particle diameter dpart in μm.		Ratio between particle surface area with and without ultrasonic treatment S_{tot_2} / S_{tot_1}	Saturation concentration SC_2 in wt.-% rel. to polym. conc.	Ratio between saturation concentration with and without ultrasonic treatment SC_2/SC_1
	Without ultrasonic treatment	After ultrasonic treatment			
P([IB-AA]-r-AA)-1 (82 % AA)	0,58	0,32	1,8	~ 2	6,7
PMAA-g-PS (71 % MAA)	0,64	0,52	1,23	~ 1,5	4,1
C16-PEO14000-C16 HEUR	3,22	0,27	11,9	~ 12	80

The comparison of the experimentally measured diameter dpart of the polymer coated particles which were obtained by application of ultrasonification (column 3 in Tab. 2) and without ultrasonification (column 2 in Tab. 2) shows that smaller particles resulted from the ultrasonification; this was to be expected since ultrasonic treatment is known to cause a breaking of agglomerates/aggregates present in pigment slurries.

Whereas the particle surface area Stot increases upon ultrasonic treatment by about a factor of 1,2 (minimum) and up to a factor of about 12 (see column 4 of Tab. 2), the saturation concentrations SC as derived from the experimental curves Fig. 1 – 3 is 4 to 80 times higher for the ultrasonically treated systems as compared to the non-treated systems (see column 6 of Tab. 2); in other words, the SC ratio is about three to seven times larger than the Stot ratio (compare columns 4 and 6 in Tab. 2). This indicates that the amount of polymer adsorbed per unit of the particle surface after ultrasonic treatment is higher as compared to non-treated samples.

The thicknesses of the adsorbed polymer layer as obtained for the different amphipolar copolymers under conditions of ultrasonic treatment in comparison to the systems without ultrasonic treatment are compiled in Tab. 3. The thicker adsorption layers observed for the ultrasonically treated systems confirm that an activation of the pigment surface occurs by the action of ultrasonic power.

Table 3

Thicknesses d of the adsorption layer of the amphipolar copolymer on TiO$_2$ for ultrasonically treated and
non-treated dispersions as calculated on the basis of the saturation concentration SC obtained from
the ESA measurements (see Table 2)

Amphipolar Copolymer	Thickness d of the adsorption layer without ultrasonic treatment, nm.	Thickness d of the adsorption layer after ultrasonic treatment, nm.	Ratio between the thicknesses of treated and non-treated samples
P([IB-AA]-r-AA)-1 (82 % AA)	1,5	8	5,3
PMAA-g-PS (71 % MAA)	1,5	7	5
HEUR C16-PEO14000-C16	3	11	3,7

A general conclusion that can be drawn from the data compiled in Tab. 3 is that the increasing of the thickness of the polymer adsorption layers upon ultrasonic treatment is confirmed from both the information obtained from the ESA measurements and from the calculations of the particle surface.

The almost tenfold increase of the particle diameter dpart as compared to the diameter of the starting material in case of the HEUR additive without ultrasonification (see Tab. 2) can only be explained by agglomerate formation. The fact that the measured particle diameter of the HEUR coated TiO_2 as obtained with ultrasonic treatment is even smaller than the specified diameter of 0,3 μm of the starting material (see Exp. Part) drastically illustrates the effect of the ultrasonic power. As a consequence of this pronounced effect of ultrasonification, the largest increase in the particle surface area is obtained (ratio S_{tot2}/S_{tot1} = 11,9).

The particle diameter and surface area of the TiO2 dispersions stabilized by PMAA-g-PS do not show such a pronounced difference between the ultrasonically treated and non-treated system and is also smaller than for the P(IB-AA-r-AA) polymer (see Tab. 2). This is also reflected from Fig. 2 which shows that the saturation concentration is already reached for comparatively low polymer concentrations which are much lower than measured for the other polymers (see Fig. 1 and 3).

This behaviour of the TiO_2/PMAA-g-PS system can be explained by the micelle adsorption model, *i.e.*, the deposition of polymer micelles (core of PS grafts and shell of PMMA backbone) onto the polymer double layer initially formed around the pigment particle [10, 11]: First, the hydrophilic, polyelectrolyte polyacrylic acid chains anchor through the carboxylic groups on positive sites of the TiO_2 surface resulting in the formation of a polymer monolayer with a relatively apolar surface, followed by deposition of further graft copolymer through interaction of the PS grafts with the firstly formed monolayer. Subsequently, micelle adsorption and layer thickening takes place, finally resulting in larger particles than observed with the other amphipolar copolymers.

Conclusions

ESA measurements have shown that ultrasonic treatment of TiO_2 pigment dispersions in aqueous solutions of amphipolar copolymers significantly effects the pigment surface modification and enhances the dispersion stability. The effect of the ultrasonic treatment is dual in that not only a finer particle dispersion but also an activation of the particle surface is achieved in the first place. The activated surface allows for a better copolymer-pigment interaction leading to firmly bonded and thicker polymer adsorption layers. Thus the ultrasonic treatment in combination with the employing of specially designed amphipolar copolymers opens new prospectives to modify the pigment surface more efficiently.

Acknowledgements

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