MODIFICAÇÃO DE SUPERFÍCIES DE NANOPARTICULAS DE DIÓXIDO DE TITÂNIO COM COPOLÍMERO DE ÁCIDO ACRÍLICO / ISOBUTILENO SOB TRATAMENTO ULTRA-SÔNICO

SURFACE MODIFICATION OF TITANIUM DIOXIDE NANOPARTICLES WITH ACRYLIC ACID/ISOBUTYLENE COPOLYMER UNDER ULTRASONIC TREATMENT

ПОВЕРХНОСТНАЯ МОДИФИКАЦИЯ НАНОЧАСТИЦ ДИОКСИДА ТИТАНА С СОПОЛИМЕРОМ АКРИЛОВОЙ КИСЛОТЫ/ИЗОБУТИЛЕНА ПРИ УЛЬТРАЗВУКОВОЙ ОБРАБОТКЕ

BULYCHEV, Nikolay A.^{1, 2}; RABINSKIY, Lev N.^{3*}

¹ P.N. Lebedev Physical Institute of the Russian Academy of Sciences, Department of Luminescence, 53 Leninskiy Ave., ZIP code 119991, Moscow – Russian Federation

² Moscow Aviation Institute (National Research University), Department of Physical Chemistry, 4 Volokolamskoe Highway, ZIP code 125993, Moscow – Russian Federation

³ Moscow Aviation Institute (National Research University), Department of Material Research, 4 Volokolamskoe Highway, ZIP code 125993, Moscow – Russian Federation

* Correspondence author
e-mail: rabinskiy@mail.ru

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RESUMO

A influência do tratamento ultra-sônico da solução do copolímero do bloco em sua interface sólido-líquido da foi investigada em detalhe. A modificação da superfície de nanopartículas de dióxido de titânio em dispersões aquosas de copolímero de ácido acrílico / isobutileno especialmente feito à medida por tratamento ultra-sônico foi estudada para se obter novas abordagens para a criação de materiais compósitos híbridos ou revestimentos poliméricos. A modificação de superfície do pigmento pelo copolímero acima foi investigada comparativamente a respeito da adsorção convencional como contrastado a um procedimento assistido do tratamento ultra-sônico. O curso e a eficiência da adsorção do polímero na superfície do pigmento foram quantificados por medições de amplitude sonora eletrocinética. A eficiência mais elevada do revestimento de superfície do pigmento pelo copolímero como conseguido pelo tratamento ultra-sônico em comparação com a adsorção convencional é uma consequência da ativação ultrassonicamente induzida da superfície do pigmento. Duas vias da perspectiva da utilização dos efeitos descobertos para a criação de materiais compostos orgânico-inorgânicos são antecipadas: as nanopartículas podiam primeiramente ser tratadas pelo ultra-som na presença de polímeros e assim criar uma superfície que modifica o revestimento e a segunda opção é um arrastamento das nanopartículas na matriz do monômero que pode mais tarde ser polimerizado produzindo um polímero com nanopartículas imobilizadas.

Palavras-chave: *modificação de superfícies, ultra-som, pigmentos, polímeros*

ABSTRACT

The influence of the ultrasonic treatment of block copolymer solution on its solid-liquid interface behavior was investigated in detail. The surface modification of titanium dioxide nanoparticles in aqueous dispersions of specially tailor-made periodic acrylic acid/isobutylene copolymer by ultrasonic treatment was studied in order to get new approaches for the creation of hybrid composite materials or polymer coatings. The pigment surface modification by the above copolymer 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 were quantified by electrokinetic sonic amplitude measurements. The higher efficiency of the pigment surface coating by the copolymer as achieved by ultrasonic treatment in comparison to conventional adsorption is a consequence of ultrasonically induced pigment surface activation. Two perspective avenues of the utilization of the discovered effects for creation of organic-inorganic composite materials are anticipated: the nanoparticles could first be treated by ultrasound in the presence of polymers and

so create a surface modifying coating and the second option is an entrainment of the nanoparticles into the monomer matrix which can be polymerized afterward yielding a polymer with immobilized nanoparticles.

Keywords: surface modification, ultrasound, pigments, polymers.

АННОТАЦИЯ

В статье детально изучено влияние ультразвуковой обработки раствора блок-сополимера на границы его раздела между жидкой и твёрдой фазами. Исследовано поверхностное модифицирование наночастицы диоксида титана в водных дисперсиях специально изготовленного периодического сополимера акриловой кислоты/изобутилена методом ультразвуковой обработки для того, чтобы выработать новые подходы к созданию гибридных композиционных материалов или полимерных покрытий. Проведено сравнение модификации пигмента с использованием упомянутого ранее сополимера и обычной адсорбции. Ход и эффективность полимерной адсорбции на поверхности пигмента определялись измерением электрокинетической звуковой амплитуды. Большая эффективность покрытия поверхности пигмента сополимером с помощью ультразвуковой обработки по сравнению с обычной адсорбцией является следствием ультразвуковой активации поверхности пигмента. Предлагается два пути применения данного эффекта для создания органических-неорганических композитных материалов: наночастицы могут быть обработаны ультразвуком при наличии полимеров и, таким образом, создать модифицирующее покрытие; второй вариант – это вовлечение наночастиц в мономерную матрицу, которая впоследствии может быть полимеризована с образованием полимера с неподвижными наночастицами

Ключевые слова: поверхностное модифицирование, ультразвук, пигменты, полимеры.

1. INTRODUCTION

The homogeneous dispersing of pigments is essential in coatings formulations. For producing aqueous pigment dispersions, many approaches have been described in the literature (Netz and Andelman, 2003; Zubov *et al.*, 2004; Bulychev *et al.*, 2004). It was shown (Ioni *et al.*, 2011; Burkhanov *et al.*, 2014; Rudnev *et al.*, 2014) that highly stable dispersions are obtained by ultrasonic treatment of pigment slurries in aqueous solutions of polymer surfactants. Recent studies (Bulychev *et al.*, 2008; Kirilina *et al.*, 2009) 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 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 an amphiphilic copolymer of well-defined structures by ultrasonic treatment. Such copolymers are characterized by special sequences of hydrophilic and hydrophobic units, which result

in specific pigment-polymer interactions and stabilizing properties (Ivanov *et al.*, 2017; Bulychev *et al.*, 2018f). The effect of the ultrasonic treatment on the deposition of the stabilizer copolymer is discussed in the context of the various copolymer architectures. The introduction must clearly state the problem, the reason for doing the work, the hypotheses or theoretical predictions under consideration, and the essential background. It should not contain equations or mathematical notation. A brief survey of the relevant literature so that a non-specialist reader could understand the significance of the presented results.

2. MATERIALS AND METHODS

As solid material, the titanium dioxide rutile pigment Kronos 2310 with particle size 0.3 μm and breadth of the particle size distribution of 60 nm was employed as received. The PiBA-PAA block copolymers of various well-defined structures, molecular weights, and narrow polydispersities, were synthesized by controlled radical polymerization as described (Bulychev *et al.*, 2004). This method enables to synthesize amphiphilic copolymers with a desirable length of hydrophilic and hydrophobic blocks. The copolymers were characterized by size exclusion chromatography.

For the preparation of the aqueous

dispersions, the copolymers were predissolved in THF as a solution aid (5 wt.-%), then this polymer solution was introduced into the distilled water (pH = 7) together with the pigment (THF/water: 1/9 v/v). This procedure prevents the precipitation of the PiBA-PAA copolymers. Dispersing of the pigment was first achieved by means of a laboratory stirrer (700 rpm for 10 min). When ultrasonification was applied, the system was subsequently treated with ultrasound for 2 min with an ultrasonic generator Branson Sonifier B-12 with the actual power of 1,5 W/cm². During ultrasonification, the polymer is being coated with the copolymer, and the THF evaporates.

Colloidal stabilization of the aqueous dispersions was monitored by sedimentation measurements of 1% dispersions of CuPc and TiO₂. For sedimentation measurements, the obtained dispersions were poured into test-tubes, and the sedimentation kinetics were monitored by following the borderline between the turbid and the transparent zones; the half-time of the sedimentation, i.e., the period of time until this borderline reaches 50% of dispersion height in the test-tube was used as a measure of the sedimentation stability. The pigment-polymer interaction and the polymer adsorption layer formation were investigated by electrokinetic sonic amplitude (ESA) measurements as described elsewhere (Bulychev *et al.*, 2008). ESA measurements were performed with an Accoustosizer 2 instrument. The particle size was measured by ESA (Bulychev *et al.*, 2008). The dynamic mobility (μ D) can be determined with an accuracy of $\pm 1\%$.

The critical micelle or aggregate concentration (CMC or CAC) of polymer solutions was controlled according to the ring-tear-off technique with a Tensiometer K-12 device (Kruss, Germany).

3. RESULTS AND DISCUSSION:

Data reported in the literature (Nikiforov *et al.*, 2016; Krasovskii *et al.*, 2018; Bulychev *et al.*, 2018a, 2018b, 2018c, 2018d, 2018; Kirichenko *et al.*, 2018a, 2018b, 2018c; Averyushkin *et al.*, 2018a, 2018b; Asratyan *et al.*, 2018; Dyakov *et al.*, 2018), showed that mechanical, in particular, ultrasonic treatment of aqueous dispersions of pigments in the presence of polymeric stabilizers leads to a significant enhancement of the stability of these

dispersions as compared to dispersions prepared without ultrasonic treatment. It was proven by IR-analysis that the thickness and stability of the polymer adsorption layers were increased and improved by the ultrasonification. Parameters of polymer adsorption layers affected by the ultrasonic treatment were investigated (Bulychev *et al.*, 2008). However, the effect of the ultrasonic treatment on the pigment-polymer interaction and polymer adsorption, especially for novel tailor-made amphipolar copolymers is still obscure and needs further investigation for the better elucidation of the phenomena observed.

First, sedimentation measurements for TiO₂ aqueous dispersions stabilized by a series of tailor-made amphipolar copolymers containing PiBA and PAA segments in the presence and absence of ultrasonic treatment have been carried out. These data are presented in Table 1.

First, as one can see from Table 1, all employed copolymers allow obtaining pigment dispersions even in the absence of ultrasonic action while recent data on the application of PMVE containing block copolymers showed the impossibility to obtain dispersions without mechanical treatment (Bulychev *et al.*, 2004). It could be ascribed to that fact that THF used as a polymer solvent in the present study is known to create micelles with water and so provide the transport of a polymer to the pigment surface. Second, 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 block length ratio; this is in accordance with previously discussed constitutional effects (Bulychev *et al.*, 2004). Third, there is a distinct effect of the pigment surface nature on the polymer structure acting as the best stabilizer: for hydrophilic TiO₂ dispersions, PiBA₁₇ – PAA₉₇ with long PAA block showed good stabilization.

ESA measurements of aqueous dispersions of TiO₂, stabilized by block copolymers of PiBA-PAA, give quantitative information about the process of adsorption of polymers as reflected first from the dependence of the dynamic mobility μ on the relative polymer concentration (Bulychev *et al.*, 2008) as shown in Fig. 1 and 2, and second from the comparison of this dependency for systems

without and with ultrasonic treatment.

As one can see from the comparison of Fig. 1 and 2, ultrasonic treatment has a distinct effect on the behavior of the particulate pigment-polymer suspension. Without ultrasonic action, the formation of a polymeric adsorption layer on the pigment surface seems to be reached at 1 wt.-% PiBA₁₇ – PAA₉₇ in relation to the pigment concentration (saturation concentration as indicated by the unchanged dynamic mobility with a further increase of polymer concentration). In the presence of ultrasonic action, first the initial dynamic mobility of the pristine TiO₂ is much higher, and the saturation concentration of polymer is only reached at about 5 %. Further addition of polymer does not affect the dynamic mobility. The decrease of the dynamic mobility after the addition of small amounts of a polymer is in agreement with the data obtained for PS-PAA block copolymers (Andreev and Gridina, 2016).

Obviously, the ultrasonic action not only increases the pigment surface by creating a more fine dispersion but also activates the pigment surface leading to ultimately higher polymer adsorption in comparison to the non-treated samples (Gridina and Andreev, 2018).

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 (Kovshov et al., 2019).

The comparison of the experimentally measured diameter part of the polymer coated particles which were obtained by application of ultrasonification (column 3 in Table 2) and without ultrasonification (column 2 in Table 2) showed 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 (Korshunov et al., 2016).

The thicknesses of the adsorbed polymer layer as obtained for the TiO₂ pigment dispersions under conditions of ultrasonic treatment in comparison to the systems without ultrasonic treatment are compiled in Table 3. The thicker adsorption layers observed for the ultrasonically treated systems confirm that activation of the pigment surface occurs by the

action of ultrasonic power.

4. CONCLUSIONS:

On the basis of the data about the dynamic mobility as obtained from ESA measurements, it was possible to get more insights into the pigment-polymer interactions and the adsorption mechanism of the copolymer. For aqueous TiO₂ dispersions stabilized by PiBA-PAA copolymer, the saturation concentrations of polymer surfactants, i.e., the maximum amount of adsorbed polymer were established. A general conclusion that can be drawn from the data obtained 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.

In particular, the data allow to conclude that ultrasonic treatment of aqueous inorganic pigment dispersions is a powerful method for pigment surface modification leading first to an activation of the pigment surface; as a consequence, improvement of the pigment-polymer interaction is achieved which results in the creation of polymer adsorption layers of high thickness. Thus, the ultrasonic treatment enables to obtain stable and high-dispersed pigment suspensions with modified pigment surface; this method opens new perspectives to modify the pigment surface more efficiently. It was shown, that using polymer surfactant in combination with ultrasonic action can significantly improve the quality of dispersed systems.

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Table 1. Sedimentation stability of TiO_2 aqueous dispersions stabilized by PiBA-PAA block copolymers

Polymer	Suspension stability (half-time of the sedimentation, days)	
	Without mechanical treatment	After ultrasonic treatment
PiBA ₇₂	0.2	4
PAA ₂₈	2	10
PiBA ₅₃ – PAA ₄₉	2	14
PiBA ₅₃ – PAA ₂₆	0.1	1
PiBA ₁₇ – PAA ₉₇	3	30
PAA ₁₇ – PiBA ₇₂ – PAA ₁₇	0.3	7

Table 2. Effect of ultrasonic treatment on the particle diameter d_{part} , and effect of ultrasonic treatment on the increase of the particle surface area (S_{tot}) as well as on the saturation concentration (SC) of added amphipolar copolymer as expressed by the corresponding S_{tot} and SC ratio; the indexes 1 and 2 refer to the non-treated (1) and ultrasonically treated (2) sample.

System	Averaged particle diameter d_{part} in μm .		Ratio between particle surface area with and without ultrasonic treatment $\frac{S_{\text{tot } 2}}{S_{\text{tot } 1}}$	Ratio between saturation concentration with and without ultrasonic treatment SC_2/SC_1
	Without ultrasonic treatment	After ultrasonic treatment		
TiO_2 + PiBA ₁₇ – PAA ₉₇	1,2	0,6	2	5

Table 3. Thicknesses d of the adsorption layer of the amphipolar copolymer on TiO_2 and CuPc surface 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).

System	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
TiO_2 + PiBA ₁₇ – PAA ₉₇	5.5	13.6	3.2

Figure 1. Dependence of the dynamic mobility on the relative concentration of PiBA₁₇ – PAA₉₇ for 1 wt.-% TiO₂ aqueous dispersion without ultrasonic treatment

Figure 2. Dependence of the dynamic mobility on the relative concentration of PiBA₁₇ – PAA₉₇ for 1 wt.-% TiO₂ aqueous dispersion after ultrasonic treatment