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Prospects for the use of paraffin-based O/W Pickering emulsions for the production of superhydrophobic coatings

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The paper presents information on the method for producing paraffin-based O/W Pickering emulsions stabilized by SiO_2/MWCNTs and superhydrophobic coatings based on them. It has been shown that the most effective way to treat building materials (fine-grained concrete and pine wood) with such emulsions is impregnation. Samples of substrates with an average contact angle of about 130° were obtained; the best result was achieved on wood treated by immersion — a contact angle of 152.3°, a rolling angle of less than 10°, which is typical for superhydrophobic coatings.

Keywords: stabilization of dispersions, multi-walled carbon nanotubes, decoration of the side walls of nanotubes with silica nanoparticles, synthesis of nanoparticles.

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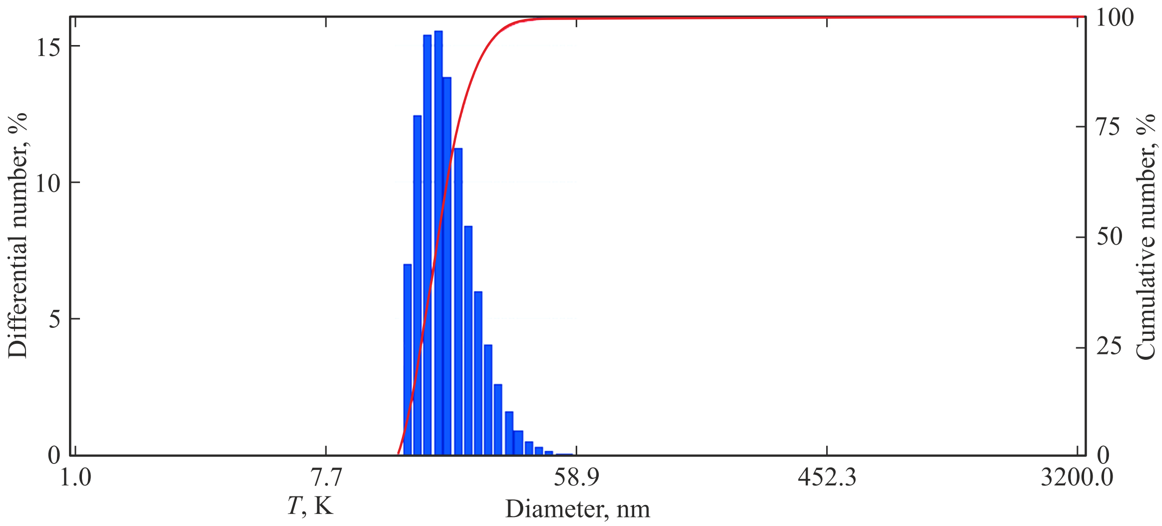
1. Introduction

Pickering emulsions are dispersions stabilized by solid particles fixed at the oil-water interface [1]. Depending on the material and shape of the particles (colloidal silicon dioxide, titanium dioxide nanoparticles, carbon nanotubes, clay particles, etc.) it is possible to obtain highly concentrated colloidal systems with different properties, characterized by different stability, resistance to changes in the pH of the environment and the introduction of electrolyte additives [2,3]. According to [4], in the case of direct paraffin emulsions with concentrations below 10 wt%, production temperature 70−75°C and the introduction of silicon dioxide nanoparticles as a stabilizer it is possible to obtain submicron paraffin particles with a diameter of 450−460 nm. In our opinion, the emulsion of similar dispersion, stabilized by multiwalled carbon nanotubes (MCNTs), the surface of which is decorated with silica nanoparticles, by analogy with papers [5,6], will be a suitable basis for creating superhydrophobic anti-icing coatings. In this case, particles SiO_2 attached to the walls of MCNTs will increase their wettability and dispersibility in water [7]. The increase in aggregative stability of such emulsions during stabilization with SiO_2/MCNT structures is explained by the fact that the hydrophilic surfaces of decorated tubes (particles SiO_2 attached to the walls) will be adsorbed on the surface of paraffin droplets from the side of the aqueous phase, forming a protective layer that prevents coalescence. On the contrary, the original hydrophobic carbon nanotubes will be drawn into the paraffin droplets without forming a protective layer.

The superhydrophobicity of the finished coating will be realized due to the hydrophobic nature of the paraffin itself in combination with the multimodal roughness formed by the presence of branched structures of SiO_2/MCNTs on the surface of the paraffin particles. Thus, a number of sources [8–11] shows how similar superhydrophobic coatings can reduce the ice adhesion to the surface, as well as create conditions under which the time of drop sliding over the surface is not enough for it to freeze and form ice. Besides, articles [12–14] proposed the idea of obtaining a three-layer superhydrophobic xerogel coating based on carbon nanoparticles. This paper is an attempt to adapt the top, hydrophobic layer of the above coating for practical needs. According to our assumptions, silica nanoparticles will not only enhance the adhesion of carbon nanotubes to the surfaces of building materials, but will also make them more resistant to frost condensation on the smooth side surfaces of CNTs. Additional large-scale studies are planned to study the anti-icing properties of the coating. Thus, the purpose of this paper was to study the possibility and prospects of synthesizing direct Pickering emulsions based on paraffin of stabilized SiO_2/MCNTs in order to obtain superhydrophobic anti-icing coatings.

2. Experiment

The synthesis of silica nanoparticles necessary for decorating the side surfaces of MCNTs (to obtain SiO_2/MCNTs) was carried out using the sol-gel method [15] at room temperature: hydrolysis of tetraethylorthosilicate (TEOS) in water-ethanol solution followed by dropwise addition of ammonium hydroxide as a catalyst for the polycondensation reaction. The ratios of components were taken according to [15] for sample № 2 (ethanol 4 M, bidistilled water 13.4 M, TEOS 0.045 M and 14 M NH_3), with the difference that ultrasonic treatment was not carried out during synthesis. As a result, after 18 h of maturation a sol with a mass concentration of SiO_2 of about 4 mg/ml was



Size distribution of silica particles.

Results of measurements of the contact angle of wetting of the obtained coatings

Composition of emulsion	d_{av}, μm	Substrate	Method of coating producing	θ_{av}, deg ($1 \to 10$ s)
Control sample (uncoated)	–	MB PW	–	$0 \to 0$ $102.5 \pm 5.4 \to 95.1 \pm 5.9$
paraffin 5% + SiO_2/MCNT	3.6 ± 0.6	FGC PW	Emulsion sputtering	$12.4 \pm 2.8 \to 0$ $125.5 \pm 26.7 \to 111.5 \pm 26.0$
		FGC PW	Immersion into emulsion	$129.7 \pm 5.9 \to 129.1 \pm 6.4$ $129.5 \pm 24.1 \to 128.6 \pm 24.6$

formed. The granulometric composition of the resulting silica sol was determined on DelsaNano C particle size analyzer using the dynamic light scattering method. The measurement was carried out at temperature 23.1°C in ethanol (refractive index 1.3611, viscosity 1.1389 cP). The size distribution of synthesized silica particles is shown in the Figure.

The average particle diameter was 20.8 ± 5 nm (percentiles D10 = 15 nm, D50 = 18.8 nm, D90 = 26.2 nm). In addition to silica nanoparticles, the sample contained hydrolyzed TEOS molecules with a diameter of about 1 nm (not shown in the Figure). Compared to the silica sol obtained in the paper [15], with an average particle size 20.5 ± 0.7 nm, our silica sol has a wider distribution 20.8 ± 5 nm.

SiO_2/MCNTs were prepared by holding 100 mg of carbon tubes (Taunit-M, „NanoTechCenter") in 5 ml of silica sol (diluted with ethanol to concentration of 0.8 mg/ml) for 1 day, followed by evaporation of the solvent.

Direct Pickering emulsion with mass concentration of 5% was obtained by dispersing 25 g of molten paraffin grade P-2 (JSC „Slavneft Yaroslavnefteorgsintez") and 50 mg of SiO_2/MCNT in 475 ml of bidistilled water on the MK module of the IKA magicLAB colloid mill (setting angle 180°, rotation speed 16000 rpm, water temperature 70°C) for 2 min. Paraffin was added to aqueous medium that already contained MCNTs predispersed for 1 min SiO_2. The average particle size of the emulsion, d_{av}, μm, was determined on DelsaNano C particle size analyzer using the dynamic light scattering method.

The emulsion was applied to substrates made of fine-grained concrete (FGC) and pine wood (PW) by sputtering with DEXTER POWER spray gun (power 600 W, pressure 0.3 bar, nozzle diameter 2.5 mm) from a distance of 15 cm. As an alternative method for obtaining the coating the immersion of the substrate in the emulsion for 24 h was chosen. The values of the contact angle of wetting of the resulting coatings (θ_{av}) with distilled water in 1 and 10 s after the droplet touched the surface were determined on DSA-20E goniometer (8 parallel measurements, the contour of the droplets was processed by the tangential method), the results are presented in the Table.

3. Conclusion

Discussing the results obtained, we can conclude that sputtering the emulsion is ineffective compared to immersion (the contact angles of wetting are smaller, and the nozzle and material supply tube of the spray gun are periodically clogged with paraffin). Therefore, further adjustment of the content of emulsion components, subsequent determination of its optimal consumption and refinement of the sputtering technology are necessary. At the same time, treating the surface of wood and concrete by immersion for a day into paraffin-based Pickering emulsion, stabilized SiO_2/MCNT, makes it possible to hydrophobize their surface, as a result of which drops of water that fall on the surface are not absorbed into the substrate and their contact angle practically does not change with time; however, such a coating is extremely heterogeneous. Thus, the largest recorded contact angle on the resulting coating (wood substrate) was 152.3° with roll-off angle less than 10°, the smallest — 111.9°, no droplet rolled off at any angle of inclination. The results obtained are due to the fact that the roughness of the resulting coating is heterogeneous and strongly depends on the processes of lifting (floating) and fixing paraffin particles on the substrate, which, in turn, are affected by their size, density, concentration and temperature of the emulsion, as well as open porosity and water absorption of the substrate. The study of the influence of the above factors on the surface and hydrophysical properties of coatings will be the subject of further study. It can be concluded that the synthesis of direct paraffin-based Pickering emulsions, stabilized SiO_2/MCNTs, is possible and promising in order to obtain superhydrophobic anti-icing coatings.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S.U. Pickering. J. Chem. Soc. **91**, 2001 (1907). https://pubs.rsc.org/en/content/articlepdf/1907/ct/ct9079102001
[2] B.V. Pokidko, D.A. Botin, M.Yu. Pletnev. Vestn. MITKhT **8**, *1*, 3 (2013). (in Russian). https://www.finechem-mirea.ru/jour/article/viewFile/646/692
[3] P.A. Demina, D.O. Grigoriev, G.M. Kuzmicheva, T.V. Bukreeva. Kolloid. zhurn. **79**, *2*, 142 (2017). (in Russian).
[4] O.S. Gorbachevsky, M.Yu. Koroleva, E.V. Yurtov. V sb. Uspekhi v khimii i khimicheskoj tekhmologii (PKhTU im. D.I. Mendeleeva) **29**, *6*, 118 (2015). (in Russian). https://www.muctr.ru/upload/iblock/bfc/bfc233630e82772f760acde13d430961.pdf
[5] E.S. Trapeznikova, N.A. Makarov. V sb. Uspekhi v khimii i khimicheskoj tekhmologii (PKhTU im. D.I. Mendeleeva) **34**, *5*, 92 (2020). (in Russian). https://www.muctr.ru/upload/iblock/a74/a7440aec8a73022bd62a728910f77925.pdf
[6] M. Javed, S.M. Abbas, S. Hussain, M. Siddiq, D. Han, L. Niu. Mater. Sci. Energy Technol. **1**, *1*, 70 (2018). https://doi.org/10.1016/j.mset.2018.03.002
[7] B. Bharti, R. Kukobat, D. Minami, K. Kaneko. Colloids. Interface Sci. Commun. **3**, 13 (2014). https://doi.org/10.1016/j.colcom.2015.03.001
[8] F. Sotoudeh, S.M. Mousavi, N. Karimi, B.J. Lee, J. Abolfazli-Esfahani, M.K.D. Manshadi. Alexandria Eng. J. **68**, 587 (2023). https://doi.org/10.1016/j.aej.2023.01.058
[9] Z. Li, M. Cao, P. Li, Y. Zhao, H. Bai, Y. Wu, L. Jiang. Matter. **1**, *3*, 661 (2019). https://doi.org/10.1016/j.matt.2019.03.009
[10] W. Huang, Q. Ye, C. Ren, Y. Lu, Y. Cai, W. Zhang, J. Huang. Front. Mater. Sci. **16**, *4*, 220626 (2022). https://doi.org/10.1007/s11706-022-0626-4
[11] Y. Ma, J. Zhang, G. Zhu, X. Gong, M. Wu. Mater. Design **221**, 110897 (2022). https://doi.org/10.1016/j.matdes.2022.110897
[12] M.K. Eseev, A.A. Goshev, S.N. Kapustin, Y.V. Tsykareva. Nanomater. **9**, *11*, 1584 (2019). https://doi.org/10.3390/nano9111584
[13] M.K. Eseev, S.N. Kapustin, D.S. Lugvishchuk, V.Z. Mordkovich, N.L. Lyakh. Tech. Phys. Lett. **46**, *11*, 1120 (2020). https://doi.org/10.1134/S1063785020110206.
[14] S. Kapustin, S. Zabolotny, M. Eseev, Y. Tsykareva. Crystals **12**, *10*, 1501 (2022). https://doi.org/10.3390/cryst12101501
[15] K.S. Rao, K. El-Hami, T. Kodaki, K. Matsushige, K. Makino. J. Colloid. Interface Sci. **289**, *1*, 125 (2005). https://doi.org/10.1016/j.jcis.2005.02.019

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