Advanced Powder Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Process chain and characterisation of nanoparticle enhanced composite coatings

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A R T I C L E I N F O

Article history:
Received 25 January 2015
Received in revised form 7 September 2015
Accepted 14 September 2015
Available online xxxx

Keywords:
Composite coatings
Nanoparticles
Doctor blade
Contact angle
Easy to clean

A B S T R A C T

The structure and the application properties of complex nanoparticulate coatings depend on the entire process chain, i.e. the nanoparticle production, the stabilization, the formulation and the further processing to a coating. Especially the formulation and the dispersing process affect the suspension characteristics and the application properties of the resultant coatings significantly. The aim of this study is to investigate the influence of mean particle size and solids content on the application properties of composite coatings for easy-to-clean surfaces. For this purpose, stable suspensions of hydrophobic alumina nanoparticles of defined particle sizes in styrene are produced. The stable suspensions are then used in a gel coat formulation and coated into sheets using a doctor blade. Finally the coatings are cured and characterised in terms of thickness, contact angle, hardness and abrasion resistance. This example shows how the use of particles with different sizes and mass contents affect the different properties of composite coatings. It is found that all analysed parameters show improved characteristics with decreasing particle size. To confirm the results in more detail and show the obvious influence of the particle distribution on the coating properties, a new AFM method was used to determine interactions on the surfaces in dependency of different formulation parameters.

1. Introduction

Composite materials act as basis for many products. Often composites are described as polymers filled with solid particles [1], composite building materials (e.g. polymer concrete) [2] or composite ceramics [3] (e.g. in industrial machine parts or dental prothesis) [4]. Additionally, coatings and gel coats containing nanoparticles, binders and additives are nanostructured composite materials as well [5]. With the use of nanomaterials, especially nanoparticles in composite materials, many product properties are generated for the first time or known product features can be significantly improved [6–8].

With the ability to create new or to enhance known properties, nanocomposites open up new fields of application, for instance in the area of mobility and lightweight construction [9,10], e.g. transparent, UV-absorbing and scratch resistant coatings [11–14]; selective induction hardening between plastic components using magnetic nanoparticles; membranes for fuel cells or CO_2 conversion by photo catalysis [15]. However, today the challenge comprises less in the preparation of nanoparticles themselves, but rather in the further formulation, functionalisation and processing of these nanoparticles [16–18].

The application of nanoparticles to provide a washbasin with an easy-to-clean coating is an example of such composite materials. The applied coating is supposed to reduce the needed effort when cleaning the surfaces, either by facilitating the dirt removal itself, or by obstructing the adherence of dirt to the surface. Thus, time and cost factors can be reduced [19].

Currently there are different approaches regarding easy-to-clean surfaces: based on the production of either hydrophilic or hydrophobic surfaces. As hydrophilic surfaces, solidified meltings of metal and/or semi-metal oxides with metal oxide particles of 20–80 nm can be used [20]. The cleaning effect is based on the improved wettability of the surface due to a water contact angle of less than 30° enabling deposited water to creep underneath the dirt which leads to an easy removal of dirt without significant force [20].

In this case a hydrophobic approach for sanitarian surfaces was chosen. The coating's hydrophobic surface repels the water and drains the surface directly taking the deposited dirt with it. The incorporation of hydrophobic nanoparticles in the outermost layer of a sanitary surface may be advantageous compared to a thin hydrophobic coating on the surface. In both cases, the composite

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http://dx.doi.org/10.1016/j.apt.2015.09.006
0921-8831/

Please cite this article in press as: J. Hesselbach et al., Process chain and characterisation of nanoparticle enhanced composite coatings, Advanced Powder Technology (2015), http://dx.doi.org/10.1016/j.apt.2015.09.006

Nomenclature

t	time (h)	γ	shear rate (s^{-1})
$x_{50,3}$	meanparticle size (nm)	η	viscosity (Pa s)
$x_{10,3}$	10% of particles are smaller than this size (nm)	Θ	static contact angle
$x_{90,3}$	90% of particles are smaller than this size (nm)	H	hardness (GPa)
E_{spez}	specific energy (kJ kg^{-1})		

is potentially eroded slowly while using and cleaning the washbasin, but the desired water repellent feature is preserved for a longer time when incorporated in the outermost layer due to a homogeneous distribution of the particles in a depth of several microns. An additional but very important effect of the nanoparticles can be an increase in abrasion and scratch resistance [21].

The systematic investigation of influencing parameters of the individual process steps on the coating structures is essential to understand the resulting application properties of coatings [22]. In this study the importance to consider the complete process chain starting with the nanoparticle production, the stabilization, the measurement of the particle size distribution, the formulation and the further processing to a coating is shown. Procedures and methods for the manufacturing of an easy-to-clean-surface are described. In order to investigate the dispersing process the stress mechanism and the operating parameters were changed. The influence of the solids content and the particle size distribution on resulting coating properties such as contact angle, hardness and abrasion resistance was examined.

2. Materials and methods

The exemplary process chain of the production of a nanoparticulate composite coating in this work consists of the particle production and functionalising, the dispersing and stabilization, the formulation and the coating and hardening. The alumina nanoparticles used in this work are produced industrially by pyrolysis and are functionalised during manufacturing. In the subsequent process step, the commercially available particles are dispersed and stabilised. This step is followed by formulating the suspension to a processible coating suspension which is then processed further to the final coating using a doctor blade, ending with a hardening process.

For an optimum adjustment of the surface properties, the influence of the process and formulation parameters of each process step along the process chain on the coating's structure formation and on the observed application properties has to be known [23]. In this paper, the influence of dispersion and stabilization is examined regarding the resulting product properties.

2.1. Materials

For the series of experiments described below hydrophobic pyrogenic nanoparticulate alumina with a specific surface of 100 ± 15 m^2/g and a primary particle size of 13 nm was used (manufacture's data sheet). In the dry state, the particles are agglomerated and partially aggregated [24]. They are functionalised with an octyl silane, in which the alkyl chain of the silane is responsible for the hydrophobic properties of the used nanoparticles. The Al_2O_3 particles are dispersed in styrene with various stabilisers of Byk Chemie to identify a suitable stabiliser. Stabiliser A is a solution of an alkylolammonium salt of a higher molecular weight acidic polymer and stabiliser B is a solution of a salt of unsaturated fatty acid polyaminamide and acid polyester. To prevent preterm polymerisation of the styrene, methyl-hydroquinone was added as inhibitor to the alumina styrene suspension. Afterwards this master batch was formulated with a styrene-containing polyester resin (company Büfa GmbH & Co. KG, Germany) and for hardening formulated with peroxide hardener.

2.2. Methods

2.2.1. Production and characterisation of the suspension

For dispersing, the media milling system TML 1 of VMA-Getzmann GmbH and two different ultrasound sonotrodes UW 2200 Sonopuls of Bandelin electronics (200 W, pre-tests) and Hielscher Ultrasonics (1000 W) were used. More information on the stress mechanisms, intensities and frequencies of a basket mill is given by Schilde et al. [25].

For dispersing, zirconia grinding beads with a diameter of 1.2 mm and 0.5 mm were used and the circumferential speed was set to 9 m/s. Additionally to this series of experiments, a vibrating mill with a grinding chamber volume of 25 ml was used for the dispersing process. 30% of the grinding chamber volume was filled with the grinding media (ZrO_2, d_{GM} = 200 μm). A frequency of 25 Hz was set for the dispersing processes, which were run for different times.

For the characterisation of the suspension dynamic light scattering, viscometry as well as optical transmission and back scattering measurement were used: The particle size distribution was determined by dynamic light scattering using a NANOPHOX from Sympatec GmbH (Germany). For each suspension sample an average of four measurements was carried out, which were evaluated with the 2nd Cumulant-method. The rheological properties were determined with a Gemini 2 (Malvern, Germany) using a cone and plate system with shear rates from 1 to 1000 s^{-1}. The stability of the suspension regarding agglomeration and sedimentation was evaluated using a Turbiscan LabExpert from Formulaction (France). With this measurement device the stability of a particulate system can be determined through the repeated scanning of a sample cell with irradiated light of the infrared range and simultaneous recording of transmission and backscattering as function of sample height and time. The changes of transmission or backscattering are based on local variations of particle concentration or global changes in particle size. Subsequently the occurring instability phenomena, which are detectable, are particle migration (sedimentation) and particle size increase (flocculation, agglomeration). Changes in the base region of the cell (e.g. 0–10 mm), the middle part (e.g. 10–30 mm) and the top (e.g. 30–45 mm) occur and can be linked to the relevant phenomena. Changes in the middle part are often based on agglomeration and changes in the bottom or the top part are based on sedimentation. However, these phenomena superpose each other and are difficult to distinguish. The optical transmission and backscattering measurement is a quite common method to identify stabilization mechanisms [26–29].

2.2.2. Production and characterisation of the composite coating

The suspensions are mixed with gel coat and hardener and then the formulated suspension are applied on sheets of plastic (release film), which allow easy removal of the sheets from the coating

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