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Studies on silicone–acrylic hybrid aqueous dispersions and corresponding silicone–acrylic nanopowders designed for modification of powder coatings and plastics

Part II – Effect of modification with silicone–acrylic nanopowders and of composition of silicone resin contained in those nanopowders on properties of epoxy-polyester and polyester powder coatings

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ABSTRACT

Epoxy-polyester and polyester coatings were modified with 3% of NP-DASI "nanopowders" consisting of core–shell nanoparticles having silicone resin of very low glass transition temperature (T_g) in the core and poly(methyl methacrylate) of high T_g in the shell. The nanopowders were obtained through spray drying of corresponding aqueous dispersions with core–shell particle structure which were synthesized in a process of emulsion polymerization of methyl methacrylate monomer in aqueous dispersions of silicone resins with different compositions resulting from different compositions of silicone monomers used for their synthesis. A designed experiment was conducted where the effect of composition of silicone resin on the properties of cured coatings was studied. It was confirmed that modification with that "nanopowder" significantly affected the properties of cured coatings, in particular impact resistance and cupping as well as surface properties. Regarding mechanical properties the influence of modification with "nanopowder" was generally more distinct for epoxy-polyester coatings than for polyester coatings. Specifically, great increase in impact and cupping resistance was observed for modified coatings and was explained by absorption of mechanical stresses by particles of low modulus silicone resin which were released from core–shell nanoparticles in the process of curing of the coatings. Other mechanical properties of cured modified and unmodified coatings (abrasion resistance, hardness, scratch resistance, elasticity and adhesion to steel) as well as appearance of the coatings (gloss and whiteness) did not differ much. Water resistance and salt fog resistance were slightly better for modified coatings. Testing the surface properties of modified coatings by XPS and AFM revealed the presence of silicone resin on coating surface what was reflected in higher contact angle and lower SFE as compared to unmodified coatings. That phenomenon was explained by migration of silicone resin to the coating surface.

1. Introduction

It is well known that nanoparticles containing low modulus polymers, specifically silicones, can significantly increase fracture toughness of polymer composites and that good dispersion of nanoparticles in the body of the composite are of great importance [1,2]. Following that concept silicone–acrylic core–shell nanoparticles have been applied as effective impact modifiers for powder coatings and plastics [3–8]. In our laboratory such impact modifiers were obtained in a form of "nanopowder" consisting of agglomerated silicone–acrylic core–shell nanoparticles by spray-drying of silicone–acrylic hybrid aqueous dispersions synthesized from silicone resin aqueous dispersions using a recently patented process [9]. Our preliminary studies confirmed [5,10–12] that addition of only 3% of such nanopowder to epoxy-polyester powder coating resulted in a very distinct increase in impact resistance, elasticity and cupping resistance without any significant change in other important coating properties (hardness, abrasion resistance). It could be explained by excellent distribution of silicone resin having very low T_g (ca. −120 °C) in the body of coating what provided resistance to stresses originated from impact or from other mechanical forces imposed on the coating during testing. As it can be seen in

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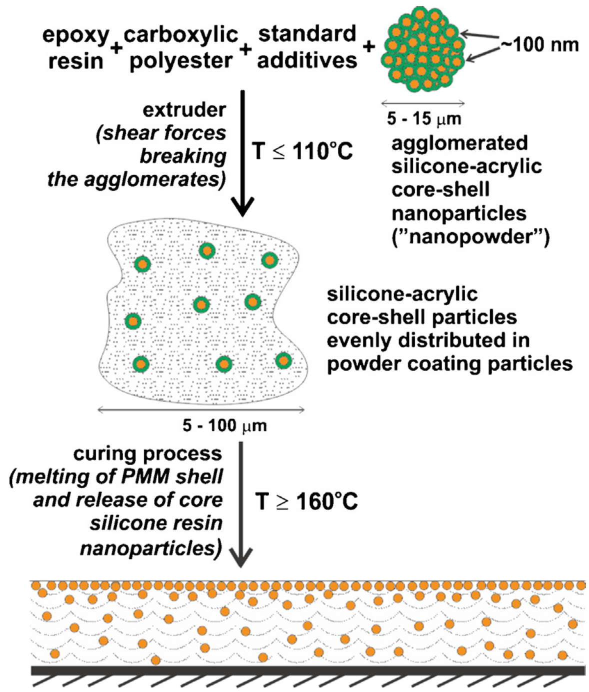

Fig. 1. Simplified scheme of the process of powder coating production with NP-DASI nanopowder added as impact modifier.

Fig. 1 presenting schematically the steps of powder coating modification with such nanopowders, during the preparation of powder coating masterbatch in the extruder at temperatures significantly lower than T_g of the methacrylic polymer core, the core–shell particles are released from agglomerates due to the shear forces without any damage of the core and become nicely distributed in the body of powder coating particles. When the powder coating is sprayed onto the metal surface and cured at a temperature of over 160 °C, i.e. significantly higher than T_g of the methacrylic polymer shell, the shell flows and the silicone resin core is released, but since the core–shell particles are separated in the body of coating there is only limited possibility of gluing of the silicone resin cores.

It was also found in our preliminary studies that TiO_2-filled coatings modified with such nanopowders showed enhanced whiteness. This unexpected benefit achieved through modification of powder coatings with silicone–acrylic nanopowders can be explained by migration of silicone resin to the coating surface resulting in changing the light reflection on the coating surface. The phenomenon of silicone resin migration to the surface of powder coatings modified with our silicone–acrylic nanopowders was fully proved by the results of XPS, AFM and SEM-EDS investigations [12–15]. It provides unique opportunity to obtain coatings of silicone-like surface, but high hardness and abrasion resistance combined with enhanced impact resistance and elasticity.

The results of our studies on the effect of starting silicone resin composition on the properties of silicone silicone–acrylic hybrid dispersions (DASI) and corresponding nanopowders (NP-DASI) obtained by spray-drying of DASI were discussed earlier [16] while in this paper the results of using those NP-DASI nanopowders of different composition of silicone resin as impact modifiers for epoxy-polyester and polyester powder coatings will be presented.

As it was explained in [16] the designed experiment was conducted in which the independent variables were contents (in wt%) of each of the compounds, i.e. octamethylcyclotetrasiloxane (D4), methyltrimethoxysilane (METMS) and methacryloyltrimethoxysilane (MATMS) in the monomers mixture used in synthesis of silicone dispersion which were assumed to correspond roughly to the resulting silicone resin composition. The experiment was designed in the form of a triangle where each corner corresponded to 100% of one of the monomers. Detailed plan of the designed experiment showing the actual situation of experimental points in that triangle was presented in Part I of our paper, so it is not repeated here.

2. Experimental

2.1. Starting materials

Epoxy resin (Epidian 012) from Chemical Company Organika-Sarzyna Poland Carboxylated polyester resin (Policen 3000T) from PPG Polifarb Cieszyn Poland, acid value – 33 – used as hardener for epoxy-polyester coatings and as main binder for polyester coatings Primid XL 552 (from EMS-Chemie AG) – used as hydroxyalkylamide crosslinker for polyester coatings TiO_2 (Rutile from Chemical Company Police Poland) – used as pigment. Benzoin from DSM and Resiflow PV 88 from Worlee Chemie GmbH – used as standard additives for powder coatings. Silicone–acrylic nanopowders applied as impact modifiers were NP-DASI samples obtained in the designed experiment described in [16].

2.2. Preparation and curing of powder coatings

For preparation of epoxy-polyester coatings epoxy resin (30 parts), carboxylic polyester hardener (70 parts), TiO_2 (30.0 parts), standard additives (1.0 parts) and, if appropriate, the NP-DASI nanopowder (3% per coating mass) were mixed in a grinder at 1000 rpm for 3 min. The resulting powder mix of starting materials was added to the Buss Ko-Knether PR-46 extruder (temp. of the screw and adapter 82 °C and 102 °C, respectively, screw rotational speed: 3.5 rpm)

For preparation of polyester coatings polyester resin (56.05 parts), hardener (2.95 parts), TiO_2 (37.0 parts), standard additives (1.0 parts) and, if appropriate, the NP-DASI nanopowder (3% per coating mass) were mixed at 1000 rpm for 3 min. The resulting powder mix was added to the extruder as described above.

It was found that the process of extrusion was clearly facilitated when the masterbatches contained NP-DASI nanopowder, indicating that the silicone resin acted as additional flow aid. The extruded masterbatches were crushed and then pulverized to yield fine powder of particle size from 5 to 85 μ. When the SEM pictures of the powder coating particles obtained using NP-DASI as additive and not containing that additive were compared it could be concluded that the particle surface was more smooth in the case of modified powder coating particles which contained NP-DASI (see Fig. 2) what confirmed our earlier observations [10,12]. This phenomenon can be explained by migration of silicone resin to the particle surface.

Powder coatings obtained as described above were deposited on both sides of steel plates using electrostatic spraying and the coated plates were placed in an oven at 180 °C for 15 min to produce smooth good looking glossy white hard coats of thickness ranging from 50 to 70 μ. More than 30 specimens were produced for each coating composition.

2.3. Testing of cured coatings

Specimens of similar coating thickness were selected for testing. The following standard properties of cured coatings were tested:

- Gloss – at 60° and 20° – according to EN ISO 2813, using Erichsen PICO GLOSS 503 apparatus
- Whiteness – using X-Rite 968 spectrometer at 0/45° geometry and at $D_{65}/10°$ illuminant value. The following parameters were measured: L^* – brightness (0–100), a^* – red/green balance