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Silicone-acrylic hybrid aqueous dispersions of core–shell particle structure and corresponding silicone-acrylic nanopowders designed for modification of powder coatings and plastics. Part III: Effect of modification with selected silicone-acrylic nanopowders on properties of polyurethane powder coatings

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ABSTRACT

Polyurethane powder coating systems consisting of polyester resin, blocked polyisocyanate and two types of "nanopowders" containing core–shell nanoparticles where the core was silicone resin of very low glass transition temperature and the shell was poly(methyl methacrylate) were examined. The blocked polyisocyanate was synthesized using biuretpolyisocyanate obtained from ureapolyisocyanate as starting material capable for blocking and ε-caprolactam as blocking agent. The surface properties of cured powder coatings were investigated using scanning electron microscopy (SEM) combined with energy dispersive spectrometry (EDS), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The surface structure was correlated with the chemical structure of the coatings and macroscopic surface behavior: contact angle, surface free energy, gloss, abrasion resistance, hardness and adhesion to the steel surface.

1. Introduction

With the progress of technology and market demand there is a growing requirement for coatings to have excellent properties, which are a consequence of new methods of synthesis and modification of base resins, selection of new curing agents and introduction of suitable functional additives e.g. nanoparticles [1,2]. The small size of nanoparticles offers two features which are both of great importance for coatings: high surface area contact with a host polymer and optical clarity of the nanocomposite. That nanotechnology has opened up exciting possibilities to improve performance attributes of coatings [3]. Materials modified with nanoparticles have different properties compared to the materials that make up individual phases, depending on the difference between intermolecular forces of the two phases. The intermolecular force between the two phases may be of chemical (e.g. functionalized polyhedral oligomeric silsesquioxanes (POSS)) or physical nature (e.g. nanoclays, TiO_2, Fe_2O_3, Al_2O_3, $BaSO_4$, CuO, ZnO, SiO_2, graphene nano-sheet, graphene oxide, carbon nanotubes, polyhedral oligomeric silsesquioxanes (POSS)) [2–4]. In recent years there is a growing interest in nanoparticles including organic or inorganic core encapsulated in a polymer shell [5–7]. Preparation of such nanoparticles is much preferable in a one-step miniemulsion polymerization [8,9]. Incorporation of nano-scale materials into polymer matrix may occur by in situ polymerization [10] or by melt-blend extrusion method [11].

In the study presented in this paper, polyurethane powder coatings were modified with nanoparticles with hard methacrylic polymer shell and soft polysiloxane core (see Fig. 1) which were obtained in the agglomerated form as "nanopowder" particles (NP-DASI) by drying of corresponding silicone-acrylic aqueous dispersions (DASI). As it was reported in detail earlier [12,13], in such silicone-acrylic core–shell nanoparticles the hard shell protects the soft core from liquidation during extrusion and guarantees good distribution of nanoparticles in the coating. Melting of the shell and release of core contents take place only at high temperature,

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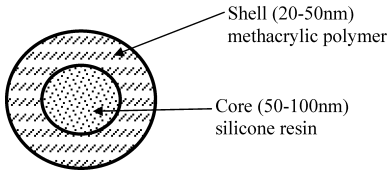


Fig. 1. The structure of silicone-methacrylic core–shell nanoparticle.

i.e. during curing process of the coating. It was anticipated that the unique structure of polysiloxane resin which constitutes the core of a nanoparticle would be the prevailing factor determining unique macroproperties of modified coatings. The results of our investigations published earlier [13] fully confirmed that assumption for epoxy-polyester and polyester powder coatings.

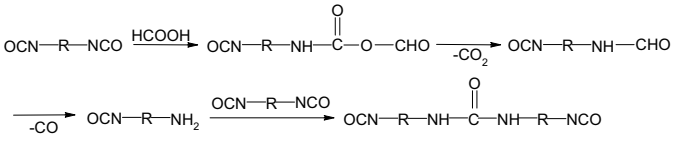
The objective of this work was to study the effect of modification with NP-DASI nanopowder containing core–shell nanoparticles with different composition of silicone resin constituting the core on the surface properties of polyurethane powder coatings.

2. Experimental

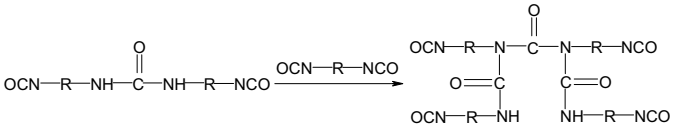
2.1. Starting materials

Isophorone diisocyanate (IPDI) – Desmodur I and Rucote 102 – polyester resin based on isophthalic acid and neopentyl glycol, acid value: 11–14 mg KOH/g, hydroxyl value: 35–45 mg KOH/g, T_g: 59 °C (RU) from Bayer A.G. (Leverkusen, Germany). Formic acid 100% from POCH (Gliwice, Poland). ε-Caprolactam (C) from Zakłady Azotowe w Tarnowie – Mościcach S.A. (Tarnów, Poland). Benzoin from Aldrich (Buchs, Switzerland). WorleeAdd 902 (acrylate resin), Resiflow PH-240 (polyacrylic resin adsorbed on silica) and WorléeAdd ST-70 (stannous octoate (II)) from Worlée-Chemie G.m.b.H. (Lauenburg, Germany). Two types of NP-DASI nanopowders containing core–shell nanoparticles (Fig. 1) with different composition of silicone resin core were selected for this study based on the results of investigations of the effect of silicone resin composition on the properties of epoxy-polyester and polyester powder coatings [13]: NP-DASI-1 which contained silicone resin of higher hydrophobicity and higher crosslinking density – T_g of core = −119.5 °C, T_g of shell = +123.3 °C and NP-DASI-2 which contained silicone resin of lower hydrophobicity and lower crosslinking density) – T_g of core = −121.7 °C, T_g of shell = +120.7 °C. For silicone resin composition see samples of the same nanopowders desigmated as NP-DASI-295 and NP-DASI-293, respectively, in our earlier paper [12].

STAGE I: synthesis of ureapolyisocyanate, temperature 60-65°C



STAGE II: biuretpolyisocyanate formation, temperature 135-140°C



STAGE III: blocking reaction of free –NCO groups by ε-caprolactam, temperature 60-65°C:

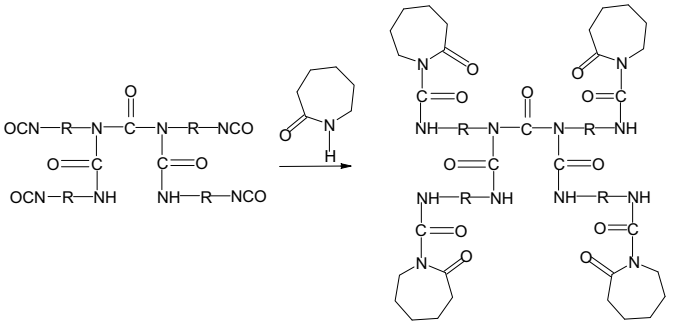


Fig. 2. Three stages of the synthesis of blocked biuretpolyisocyanate.

2.2. Synthesis of curing agent for powder coatings

Biuret bonds – containing polyisocyanate was used as curing agent. It was synthesized according to the procedure as described in details in earlier reports [14,15]. The synthesis covered three stages: synthesis of ureapolyisocyanate, synthesis of biuretpolyisocyanate, and blocking reaction (Fig. 2).

Ureapolyisocyanate was obtained in the reaction of diisocyanate and formic acid at the molecular ratio of 4:1, in the presence of dibutyltin dilaurate and triethylamine applied as catalysts (both at 0.1 wt% with respect to diisocyanate), at 60 ± 1 °C. In order to synthesize biuret linkages, the reaction mixture was heated up to 140 ± 1 °C, stirred and refluxed during 10 h. Free —NCO groups were subjected to blocking by use ε-caprolactam at the final stage. The obtained product was marked with symbol IPDI/B/C where individual segments stand for the names of the substrates used.

2.3. Preparation of powder compositions and coatings

The powder coating compositions consisted of blocked polyisocyanates, polyester resin Rucote 102 (the NCO:OH molecular ratio = 1:1), WorléeAdd 902 (1.5%), benzoin (1%), WorléeAdd ST-70 (0.5%), Resiflow PH-240 (3%) and core–shell nanoparticles in amounts 1%, 3% and 5%.

The mixture was milled and extruded in a co-rotating twin screw miniextruder EHP 2x12 Sline from Zamak (Kraków, Poland) and then pulverized to the average particle size of 60 μm. Temperature distribution in the extruder was as follows: zone I – 95 °C, zone II – 110 °C, zone III – 120 °C, adapter – 125 °C. Screw rotational speed was 25 rpm. The final powder coating was applied manually to steel and glass panels and cured at 170 °C for 30 min. The obtained compositions were marked with symbols, where individual segments stand for the names of the substrates used: e.g., IPDI/B/1N-5%/RU contains IPDI biuret, 5% of NP-DASI-1 and polyester resin Rucote 102.

Scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS) was used for assessment of the coating surface and elements distribution on the surface. The chemical composition of the coating within the depth of 10 nm from the surface was determined using X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was employed for visualizing the surface topography of the cured coatings. In order to examine the influence of modification with NP-DASI nanopowder which contained core–shell nanoparticles on the properties of polyurethane powder coatings, the measurements of the contact angle, gloss, abrasion resistance, hardness and adhesion to steel were carried out. The relationship between coating properties and NP-DASI content and type was discussed.

2.4. Measurements

2.4.1. Scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS)

The tests were performed by means of JEOL electron microscope type JSM 69-40LV in the Testing Laboratory POLMATIN, at

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