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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 I – Effect of silicone resin composition on properties of dispersions and corresponding nanopowders

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ABSTRACT

Aqueous silicone-acrylic dispersions with core–shell particle structure can be obtained in the process of emulsion polymerization of acrylic or methacrylic monomers in previously synthesized silicone resin dispersions. If the glass transition temperature (T_g) of the shell is around +120 °C or higher, drying of such dispersions leads to "nanopowders" which can be applied as impact modifiers for powder coatings and plastics due to the presence of low T_g silicone resin contained in the hybrid nanoparticles. The aim of our study was to investigate the effect of silicone resin composition on the properties of dispersions and the corresponding nanopowders what, in turn, was expected to influence the properties of powder coatings modified with such nanopowders. Silicone resin dispersions (DSI) were synthesized by emulsion polymerization of three silicone monomers: octamethylcyclotetrasiloxane (D4), methyltrimethoxysilane (METMS) and methacryloyltrimethoxysilane (MATMS) in the presence of dodecylbenzenesulphonic acid playing the role of both surfactant and polymerization catalyst. Silicone-acrylic hybrid dispersions (DASI) having core–shell particle structure confirmed by TEM were further obtained by emulsion polymerization of methyl methacrylate in DSI, and eventually nanopowders (NP-DASI) were produced by spray-drying of DASI. A designed experiment was conducted where the different proportions of D4, METMS and MATMS were used in DSI synthesis and a range of properties of DSI, DASI and NP-DASI were tested. A significant effect of starting silicone monomers composition (reflected in silicone resin structure) on dispersion particle size was observed what could be explained by differences in their hydrophobicity. SEM investigations revealed that NP-DASI were produced in the form of 1–10 μm agglomerates of round-shaped nanoparticles of ca. 120 nm in size. Two clear glass transition temperatures (T_g) of NP-DASI were identified by DSC: one attributed to silicone part – around −120 °C – and the other attributed to poly(methyl methacrylate) (PMM) part – around +120 °C. T_g attributed to silicone part decreased with increased share of D4 and MATMS in the silicone monomers composition while T_g of PMM part showed a minimum for specific composition of silicone monomers.

1. Introduction

One of the substantial problems in powder coatings technology is to develop a coating which would be impact resistant and elastic and in the same time would retain high hardness and abrasion resistance. It was proved that it is possible to achieve this goal through modification of the powder coating composition with impact modifiers applied in the form of nanopowders consisting of core–shell nanoparticles where core was silicone polymer of low T_g (around −120 °C) and shell was methacrylic polymer of high T_g (around +120 °C) [1–3]. Nanopowders were obtained from silicone-acrylic dispersions of core–shell particle structure which were synthesized by emulsion polymerization of methacrylic monomers in starting silicone polymer dispersion [4,5]. In our earlier studies we developed a novel method of synthesis of silicone-acrylic dispersion [6] and confirmed that it could be spray-dried to produce silicone-acrylic nanopowder which was proved to be effective impact modifier for epoxy-polyester powder coatings [7]. The results of those preliminary studies showed that modification of epoxy-polyester powder coatings with just 3% of such nanopowders resulted in a very significant increase in coating impact resistance and elasticity while other substantial properties

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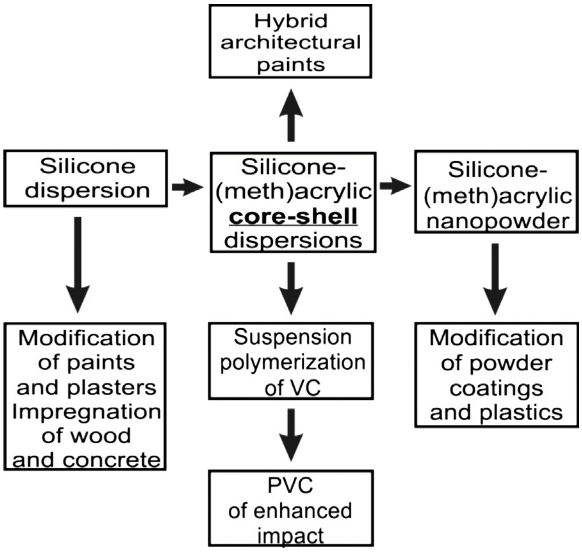

Fig. 1. The scheme of a process of making silicone-acrylic nanopowder at a semi-technical scale showing possible applications of nanopowder and of the intermediate products.

(hardness, abrasion resistance, water resistance) were not deteriorated. This was attributed to the ability of silicone part of the nanopowder particles which were evenly distributed in the coating to absorb mechanical energy of impact. It was also found that the coatings filled with TiO_2 and modified with such nanopowders showed better whiteness and brightness than non-modified ones and exhibited a "silicone touch" that is specific feature for silicone coatings. Based on the investigations of surface properties of the coatings using SEM-EDS, XPS and AFM techniques it was proved that those unique properties resulted from silicone migration to the surface [7–9]. Recently, the same nanopowders were applied as modifiers for polyurethane powder coatings [10] and it was confirmed that also in that case the silicone part of the nanopowder migrated to the coating surface. Such silicone-acrylic hybrid polymer was also proved to act as impact modifier for PVC both when added in a form of nanopowder to PVC masterbatch before extrusion [11] and when added in a form of aqueous dispersion in a process of suspension polymerization of vinyl chloride [12].

A scheme of the process that we developed comprising production of silicone-acrylic nanopowder starting from aqueous silicone polymer dispersion showing possible applications of that nanopowder and its intermediate products is presented in Fig. 1.

This paper presents the results of the first part of our broader study that was aiming at optimization of nanopowder properties in view of its application as impact modifier. In this paper synthesis and characterization of starting silicone resin dispersions of different composition, corresponding silicone-acrylic dispersions and related nanopowders will be described while the results of our studies on characterization of powder coatings modified with silicone-acrylic nanopowders of different composition will be revealed in the next submissions to this journal designated as Parts II and III.

Aqueous dispersions of polymer nanoparticles of hybrid "core–shell" structure where the core is made of a polymer A and the shell – of polymer B of different T_g are usually produced by emulsion polymerization of monomer(s) B in aqueous dispersion of polymer A [13–16], though other methods can also be applied, e.g. swelling of dispersion particles of polymer A in monomer(s) B and subsequent polymerization [17]. It was proved, based on the results of studies on synthesis of poly(acrylic-styrene-urethane) dispersions, that depending on the method used different morphologies of dispersion particles could be obtained [18].

In all emulsion polymerization processes aiming at hybrid structure of dispersion particles the phenomenon of secondary nucleation shall be avoided as it leads to the formation of mixture of separate particles of polymers A and B instead of hybrid dispersion particles. Secondary nucleation may proceed through penetration of oligomeric radicals to surfactant micelles instead of dispersion particles ("micellar nucleation") or through direct formation of new dispersion particles from growing reactive oligomers ("homolytic nucleation"). Micellar nucleation can be avoided [19] by keeping the surfactant concentration at the lowest possible level (lower than CMC – Critical Micelle Concentration) in the course of polymerization while in order to avoid homolytic nucleation the process should be carried out keeping low monomer concentration in the reaction mixture ("starve-feed" process) and in the same time $R \times N$ value should be as high as possible, where R = radius and N = concentration of starting dispersion particles, respectively [14]. Additional important condition of formation of a core–shell particle structure is that the polymer which constitutes the core has to be more hydrophobic that the one constituting the shell. Otherwise, migration of the core polymer to the particle surface may occur what may lead to damage of the core–shell structure and formation of other particle morphologies like e.g. "embedded sphere" [18].

Many core–shell dispersion systems have been developed so far following those principles and a number of them have been commercialized and used mostly as binders for coatings. Specific types of core–shell dispersions are those where the core polymer has very low T_g while the shell polymer has relatively high T_g. Due to high T_g of the shell, drying or coagulation of such dispersions does not lead to formation of continuous film, but rather powders are obtained. Such powders (or "nanopowders" – if starting dispersion particle size is around 100 nm or lower) can be used as modifiers of thermoplastic or thermoset polymers imparting higher elasticity and impact resistance to coatings or composites made of those polymers.

Especially interesting are aqueous dispersions of core–shell particle structure where the core is made of silicone resin because its T_g is exceptionally low (usually below $-100\,^\circ C$) and thus it could be expected that modification of thermoplastic or thermoset polymers with nanopowders obtained from such dispersions would result in significant enhancement of their properties. Coatings formulated using such modified polymers when applied as binders may show much improved impact resistance and elasticity [1]. Aqueous dispersions of nanoparticles with silicone core can be obtained in a two step process: (1) emulsion polymerization of silicone monomers (alkoxysilanes or/and cyclic oligosiloxanes) in water, or direct dispersing of ready-made silicone polymer or resin in water and (2) emulsion polymerization of monomer(s) (usually methacrylates, styrene or/and acrylonitrile) leading to a polymer which will constitute the shell [4,5]. After subsequent drying of such dispersions fine nanopowders can be obtained which can be used as impact modifiers for polymers and coatings.

The aim of the study presented in this paper was to investigate the effect of silicone monomers composition (corresponding to resulting silicone resin composition) on the properties of starting silicone resin dispersion (DSI), silicone-acrylic core–shell dispersion (DASI) and nanopowders produced from DASI dispersions (NP-DASI). Some of the results of those investigations were presented at international conferences and symposia [20,21].

2. Experimental

2.1. Starting materials for synthesis of DSI and DASI dispersions

Silicone monomers, i.e. octamethylcyclotetrasiloxane (D4) – from Momentive, methyltrimethoxysilane (METMS) – from Acros