



Historical perspective

Silicone-containing aqueous polymer dispersions with hybrid particle structure



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ABSTRACT

In this paper the synthesis, characterization and application of silicone-containing aqueous polymer dispersions (APD) with hybrid particle structure are reviewed based on available literature data. Advantages of synthesis of dispersions with hybrid particle structure over blending of individual dispersions are pointed out. Three main processes leading to silicone-containing hybrid APD are identified and described in detail: (1) emulsion polymerization of organic unsaturated monomers in aqueous dispersions of silicone polymers or copolymers, (2) emulsion copolymerization of unsaturated organic monomers with alkoxy-silanes or polysiloxanes with unsaturated functionality and (3) emulsion polymerization of alkoxy-silanes (in particular with unsaturated functionality) and/or cyclic siloxanes in organic polymer dispersions. The effect of various factors on the properties of such hybrid APD and films as well as on hybrid particles composition and morphology is presented. It is shown that core-shell morphology where silicones constitute either the core or the shell is predominant in hybrid particles. Main applications of silicone-containing hybrid APD and related hybrid particles are reviewed including (1) coatings which show specific surface properties such as enhanced water repellency or antisoiling or antigraffiti properties due to migration of silicone to the surface, and (2) impact modifiers for thermoplastics and thermosets. Other processes in which silicone-containing particles with hybrid structure can be obtained (mini-emulsion polymerization, polymerization in non-aqueous media, hybridization of organic polymer and polysiloxane, emulsion polymerization of silicone monomers in silicone polymer dispersions and physical methods) are also discussed. Prospects for further developments in the area of silicone-containing hybrid APD and related hybrid particles are presented.

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Abbreviations: ABS, acrylonitrile–butadiene–styrene copolymer; ABSA, alkylbenzenesulfonic acid; AFM, atomic force microscopy; APD, aqueous polymer dispersion(s); ATRP, Atom Transfer Radical Polymerization; BA, butyl acrylate; D₄, octamethylcyclotetrasiloxane; D₄^V, tetra vinyltetramethylcyclotetrasiloxane (see also: ViD₄); DPD, dissipative particle dynamics; EDS, energy-dispersive X-ray spectroscopy; FTIR, Fourier transform infrared spectroscopy; GPC, gel permeation chromatography; MA, methacrylic acid; MMA, methyl methacrylate; MPS, methacryloxypropyltrimethoxysilane; NHMA, N-hydroxymethyl acrylamide; NMR, nuclear magnetic resonance; PDMS, polydimethylsiloxane; PHMS, poly(hydrogenmethylsiloxane); PPE, poly(phenylene ether); PS, polystyrene; PTFE, polytetrafluoroethylene; PTMA, poly(methyl methacrylate); PTMG, poly(tetramethylene glycol); PVC, poly(vinyl chloride); RAFT, Reversible Addition–Fragmentation Chain Transfer; SAN, styrene–acrylonitrile copolymer; SAXS, small angle X-ray scattering; SDBS, sodium dodecylbenzenesulfonate; SEM, scanning electron microscopy; ST, styrene; XPS, X-ray photoelectron spectroscopy; TEM, Transmission electron microscopy; ViD₄, tetra vinyltetramethylcyclotetrasiloxane (see also: D₄^V); VTS, vinyltriethoxysilane.

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1. Introduction

Aqueous polymer dispersions (APD) are among the most common commercial forms of polymers. Each year ca. 7.5–8 million tons of polymers are produced and sold on a global market in a form of APD [1,2]. It corresponds to ca. 15 million tons of APD which are used in a range of applications including, inter alia, coatings, paints, adhesives, rubbers, plasters, sealants, impregnating agents, drug release systems and others. Extended review of APD applications is contained in [1]. The reasons for such widespread and still growing use of APD are not only lack of environment-related problems or easy handling and application, but also possibility of tailoring the composition and structure of dispersion particles to meet the required properties of final product. If the size of dispersion particles is lower than 100 nm, the particles can be called “nanoparticles” and specific interactions between polymeric constituents of the particle are possible on a nano scale which may result in a synergistic effect leading to unexpected new features of films, coatings or powders produced from such dispersions. If the aqueous dispersions of two different polymers (e.g., acrylic polymer and polyurethane) are blended, direct interaction between both polymers will not be possible since each will be contained in a separate particle. However,

if hybrid¹ dispersion with particles composed of both polymers is synthesized a synergistic effect can be observed [5]. Obviously, “true hybrid” particle structure where macromolecules of both polymers are truly mixed on a nano-scale is only hypothetical, but it can be expected that better compatibility of both polymers would result in better interaction between polymer chains and would then be advantageous in terms of final properties of film or coating. As it was stated in [6] “*In particular, we can expect a better compatibility and a more regular distribution of the two phases within the film material without the occurrence of significant phase segregation*”. Advantages of hybrid APD over mixtures of APD were proved in many reports, e.g., [7–11] and the general issue of heterogeneity in waterborne systems including APD was discussed extensively in a critical review paper focused mainly on polymer coatings [12].

A number of books and review papers deal with synthesis, characterization and applications of hybrid polymer materials or

¹ In a broader sense “hybrid material” means “a material that includes two (or more) moieties blended on a molecular scale” [3]. While in the relevant literature, the term “hybrid” is usually applied mostly to inorganic–organic composites [3,4], it will be used in this paper also with respect to systems of non-uniform morphology involving two or more different polymers or polymer segments, specifically those which constitute APD particles.

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