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The effect of micro and nano-sized particles on mechanical and adhesion properties of a clear polyester powder coating

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ABSTRACT

In this study, the effect of various micro and nano-sized particles on the mechanical and adhesion properties of a commercial non-pigmented polyester-TGIC powder coating was studied. Different coating formulations containing various wt.% of aluminum hydroxide (alumina) particles, TiO_2 and two different types of fumed silica nanoparticles were prepared via a two-stage process. Tensile strength measurements, DMTA analyses and vertical pull off adhesion test were conducted to evaluate mechanical and adhesion properties of the powder coating samples.

The results revealed that the mechanical properties of the powder coating samples were improved with respect to the particles loading up to 2 wt.%. The extent of this effect depends on the weight fraction and size of the particles. The fumed silica nanoparticles with dimethyl dichlorosilane treatment revealed to be more effective to enhanced mechanical and adhesion properties due to relatively better dispersion and plausible chemical interactions between silane treatment on the nanoparticles surface and polymeric matrix. The fluctuation in the mechanical properties was also observed as the particles content further increased up to 3 wt.% due to an undesirable dispersion of the particles and in turn to the presence of aggregates, air pockets as well as discontinuity in the film.

Eventually, the results revealed that pre-dispersion of nanoparticles in an appropriate solvent such as ethanol with the aid of ultrasonic irradiation, is a useful and applicable method before addition to a powder coating formulation. In fact, applying ultrasonic irradiation facilitates breaking down of nanoparticles aggregations to possible primary particles.

1. Introduction

Nowadays, due to the commercial success and growing popularity of powder coatings [1–3], there is a great demand of research work in this field [4–6]. Powder coatings present several advantages including little or no volatile organic content, high utilization rates, energy savings and elimination of hazardous waste [7,8]. Nevertheless, the mechanical properties, such as tensile strength, Young modulus, flexibility, and chemical resistance of the coating film maybe affected by the extent of cross-linking of the final cured film [9,10]. These limitations prevent powder coatings from further penetrating into many application areas of conventional solvent based coatings [11].

Furthermore, conventional powder coatings may have some shortcomings in their preparation and application performance properties [11]. For instance, in order to achieve a smooth film, coating powders must flow well at the curing temperature, and several powder coating systems not appropriate flowability as a result of their high melt viscosity. In order to improve the flowability, it is essential to use binders with low melt viscosity. It is apparent that the binders with low melt viscosity usually have low T_g values, which significantly affect powder coating storage stability and mechanical properties of the final cured product [12]. The other method to enhance mechanical properties, without binder changing, is to incorporate inorganic fillers into the coating formulations, which now for conventional organic coatings is prominent. However, applying this approach may cause; loss of transparency, tremendous increasing of coating melt viscosity and addition of appearance coating defects [13]. Moreover, large quantity of fillers must be used to obtain appropriate results, and this can change other properties such as melt viscosity and as a result of this, flowability of powder coatings. Also, it may be difficult to incorporate large quantities of fillers into powder coating compositions due to the difficulty of the dispersion process and dispersion stability problems [9].

Currently, the preparation of nanocomposite coatings has been intensely considered due to special mechanical and optical

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Table 1
Various used micro and nano-sized particles and their characteristic properties.

Materials	Trade name	Supplier	Chemical structure	Descriptions		
				BET-surface area (m^2/g)	Mean particle size	Surface modification
Silica nanoparticles	AEROSIL® R 972	Evonik, Degussa GmbH	Hydrophobic amorphous fumed SiO_2	110 ± 20	16 nm	Dimethyl dichlorosilane
Silica nanoparticles	HDK H30	WACKER Chemie AG	Pyrogenic Silica-fumed SiO_2	250 ± 20	12 nm	$-OSi(CH_3)_2-$(DMDS)
Titanium dioxide nanoparticles	UV-TITAN L230	KEMIRA	TiO_2: 87%	40	50 nm	Al, Si, Zr, Org.
Alumina	DISPERSAL P2	SASOL	Boehmite alumina Al_2O_3: 72%	260	25 μm	–

properties, and wide-spread potential applications [14–16]. Nano-sized materials have the potential to overcome many of above-mentioned disadvantages, because of their inherent small size and particle morphology. Therefore, the idea of improving the mechanical properties, by addition of small amounts of nanoparticles, without a significant effect on the melt viscosity of the coating, is highly regarded. However, the nature of powder coatings preparation process, is a key limitation for using nanoparticles, as the way they are used in conventional organic coating, where the coating's components are exposed to shear stress in the molten state in a very short time (less than 1 min). At these conditions, with respect to the nanoparticle size and attractive forces between them, proper dispersion and distribution of nanoparticles in the polymer matrix would not be achieved easily. It is worthy to note that enhancement of the coating properties by addition of nanoparticles can be obtained, when the nanoparticles are well dispersed in the polymeric matrix as the primary particle or with the possibility of chemical interactions between polymeric coatings and surface treatment of nanoparticles [16].

Nanoparticles are usually dispersed into the conventional coatings, using different methods such as; applying mechanical shear forces such as ultrasonic irradiation [17], pre-dispersion in a solvent (slurry method) [18], nanoparticles surface treatment with an appropriate silane compound [16], addition of nanoparticles in situ polymerization [19]. The aim of this study was to investigate the possibility of using slurry method (pre-dispersion in ethanol) to disperse various micro and nano-sized particles in a clear polyester/TGIC powder coating, and to study the effects of their inclusion on the mechanical and adhesion properties of the coating samples. Tensile strength measurements, DMTA analysis and vertical pull off adhesion measurement tests were used to evaluate formulated coating samples.

2. Experimental

2.1. Materials

URALAC as a carboxylated polyester resin, with 32–38 mg KOH g^{-1} acid value, T_g of 64 °C was purchased from DSM. Araldite PT 810, triglycidylisocyanurate, TGIC, EEW: 107 g $equiv.^{-1}$, 95 °C melting point, was obtained from Ciba-Geigy Ltd. and used as the polyester hardener. Flow agent, Resiflow PV5, and benzoin as a degassing agent, were supplied by Worlée and CAFFARO, respectively. Various used micro and nano-sized particles and their characteristic properties are listed in Table 1. All materials were used as received without any further purification.

2.2. Powder coatings preparation

Powder coating samples containing different types of particles, were prepared via a two-step procedure; pre-dispersion of particles in ethanol, and a standard powder coating production, respectively. In the first step, all particles were kept in a low vacuum chamber for 1 h at 120 °C and then certain amount (g) of each particle was dispersed in 50 ml ethanol via sonication (Bandelin, HD3200, KE-76 probe) by pulsation for 3× 10 min (0.7 s pulse on and 0.3 s pulse off) using power of 70 W. In this approach, the agglomerated nanoparticles are breaking down using a mechanical method such as ultrasonic irradiation in an appropriate time [17]. The suspensions were concentrated to a 50 ± 10% w/v paste using a low pressure vacuum oven via solvent evaporation. In the second step, all ingredients of various powder coating formulations (Table 2) including; the resin, hardener, degassing agent and flowing agent were weighed and then mixed together in a Lab CM6 mixture (Mixaco Co.) at mixing speed of 2000 RPM for 5 min. The pre-mixed compounds and particles' pastes were then simultaneously fed into a twin-screw lab extruder (SARONNO, EBVP 20/24 Model, OMC), under controlled heating condition – at approximately 70–100 °C – to avoid premature curing of the system. Shear forces then broke down the particles aggregates to form a homogenous dispersion which was subsequently discharged from the extruder. The hot melt materials were converted into a cool, hard, and brittle strip by passing them through cooled rollers. The final operation in the cooling stage was to crush the extrudate into small flakes around 5–10 mm in diameter, using rotating hammers fitted at the end of the cooling stage. The flakes were then pulverized in a 2M100, Retch, high-speed lab-mill to the particles size of 10–75 μm. Laser particle size analyzer, CILAS 920 was used to determine the average particle sizes of prepared powder coating samples. D_{mean} for all samples measured between 35.5 and 39.4 μm.

The powder coating samples were then applied on degreased mild steel panels (Q-panel size) using a Easy Model, from Gema, electrostatic spray gun with an output voltage of 60 kV. Subsequently, the sprayed coated samples were cured for 15 min at 180 °C. The thickness of the cured coating samples was measured to 50 ± 5 μm using an Elcometer 456 instrument.

Freestanding films were prepared by applying the powder coating samples on a pre-heated polytetrafluoroethylene (PTFE) sheet, and cured for 15 min at 180 °C. After curing, the coating's films were removed from the PTFE sheet. The thickness of the freestanding films was measured as 200 ± 20 μm.

2.3. Mechanical properties

Tensile properties of free-standing coating films were evaluated according to ASTM D2370 test practice. Rectangular tensile specimens (0.2 mm × 2 mm × 5 mm) were prepared by cutting the film to the shape. The experiments were carried out using an universal testing machine (SMT-20, Santam, Iran). The crosshead moved with a constant speed of 5 mm min^{-1}, at 23 ± 2 °C. Seven replicate samples were tested for each formulation for statistical accuracy. DMTA study was conducted on powder coating samples containing 1 wt.% of each particle using a Triton model Tritec 2000 in a tensile mode, under N_2 atmosphere. Measurement of the shear storage