Studying dispersion quality of nanoparticles into a bio-based coating

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ABSTRACT

The aim of this study was to improve performance of a vegetable oil-based coating with addition of nanoparticles. Uniform distribution of added nanoclay, nanosilica and nanoalumina is the key to ensure the increased abrasion resistance. A high speed mixer, bead mill and ultrasonic mixer were used to disperse the nanoparticles into coatings. The quality of nanoparticle dispersion in liquid coating was studied by dynamic light scattering (DLS), and in dry film by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Using a high-speed mixer with addition of glass beads resulted in exceptional dispersion of nanoparticles in coating as confirmed by the above techniques. Although, addition of nanoclay had a positive effect on drying time of coating (reducing it by 37%), it had negative effects on viscosity (increasing it by 5 times). Overall, addition of 1% nanoparticles significantly increased the abrasion resistance of modified coating after 2000 abrasion cycles in comparison with pure unmodified coatings as applied on larch wood flooring samples.

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1. Introduction

Application of coatings, such as oil finishes, made of renewable resources are increasing in the interior wood coating market as observed in many flooring distribution stores. The interests in protecting the environment, increasing safety of workers, and moving toward less fossil fuel dependent technology are the main reasons for this shift. However, vegetable oil-based finishes do not provide the scratch and wear resistance [1] that is needed for flooring applications. Addition of nanoparticles like alumina (Al_2O_3), silica (SiO_2) and zirconia (ZrO_2) have been reported to improve scratch and wear resistance of coatings [2–6]. Although alumina and silica nanoparticles improve the durability of the bio-based coatings, homogenous dispersion is crucial to attain the beneficial effect of nanoparticles addition to the coating formulation [2].

Dispersion of nanoparticles in any liquid medium is comprised of three main steps: (1) wetting: interaction of nanoparticles with coating; (2) separation: breaking down the agglomerates and aggregates to their primary particles; and (3) stabilization: preventing the formation of flocculates [7,8]. Since the surface tension of the coating (based on vegetable oil) is around 28–31 mN/m [9] which is significantly lower than the surface energy of the inorganic nanoparticles ranging from 50 to 90 mN/m [10], wetting should not be an issue when mixing inorganic nanoparticles in vegetable oil [1].

In the separation step, the goal is to overcome the interaction forces between the particles by breaking down the agglomerates [11]. There are different types of dispersion equipment that are commonly used in the coating industry for dispersing pigment, including: high-speed disk disperser, ball mill, bead mill, three-roll or two-roll mill, and ultrasonic disperser [8]. Landry et al. [12] compared a number of techniques to disperse nanoclay into a high solid UV-curable acrylate formulation and found three-roll milling, and to a lesser extent, bead milling were the best methods for dispersing nanoparticles into the 100% solid acrylate coating.

Another important step after the initial proper wetting and separation is the stabilization of nanoparticles in liquid during the storage time and before application. There are two different stabilization mechanisms: (1) electrostatic repulsion: which is mainly applicable for polar systems like water-based coatings and; (2) steric hindrance: which is suitable for nonpolar media [10]. In steric

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stabilization a long-chain additive is usually used to adsorb to the surface of nanoparticles to prevent reflocculation of particles [13].

The quality of nanoparticles distribution in liquid coatings and films can be studied by a number of advanced analytical techniques. Dynamic light scattering has been used to evaluate the nanoparticle size distribution in liquids [14–18]. The Z-average (dynamic particle size) can define the efficacy of the initial dispersing technique in breaking down the agglomerates to their primary particles in liquid coatings.

To evaluate the dispersion quality of nanoparticles in a coating's film, the following techniques have been used in previous studies: scanning electron microscopy (SEM) [19], X-ray diffraction (XRD) [20,21], field emission scanning electron microscopy (FE-SEM) [6,21], atomic force microscopy (AFM) [19,22,23], transmission electron microscopy (TEM) [5,17,18,20,23,24], confocal laser scanning microscopy (CLSM) [23], small angle neutrons size scattering (SANS) [23], and time-of-flight secondary ion mass spectrometry (ToF-SIMS) [22]. Baer et al. [22] compared a number of chemical analysis tools and reported their suitability for studying the characterization of nanoparticles. Choosing the right methods depends on accessibility and suitability of the technique, as well as the time and expertise needed for data manipulation. For example, compared to other surface analysis techniques, ToF-SIMS is the most challenging one, from its sample preparations to the data interpretation and manipulation. However, it provides very detailed information about both the surface morphology and the chemistry. The high mass features identify different molecular fragments of nanoparticles which can be used as markers in high resolution imaging of samples to ascertain distribution of particles on the surface. In addition, principle component analysis (PCA) [25] of ToF-SIMS data obtained from both imaging and spectral data, simplifies the results and eliminates the systematic variances like topography and matrix effects [26,27].

This paper is focused on finding the best method for dispersing nanoparticles into a bio-based coating and also exploring different techniques that can provide complementary and comprehensive information about the quality of nanoparticles dispersion both in liquid coatings and the dry coating film.

2. Materials and methods

2.1. Raw materials

Three different types of nanoparticles were used in this study: (1) nanoclay (Garamite 1958): (80/20 sepiolite ($Mg_4Si_6O_{15}(OH)_2\cdot 6H_2O$)/saponite ($Ca_{0.25}(Mg,Fe)_3((Si,Al)_4O_{10})(OH)_2\cdot n(H_2O)$)) treated with methyl benzyl dihydrogenated tallow, (2) nanosilica (Aerosil R 805): a hydrophilic fumed silica treated with octylsilane, and (3) nanoalumina (Aeroxide Alu C805): a highly dispersed hydrophilic fumed aluminum oxide treated with octylsilane. The coating (Secondo oil) that was used in this study was a commercially formulated coating based on natural resins, vegetable wax and refined solvent.

2.2. Dispersion of nanoparticles

Three different dispersion techniques (high speed mixer, bead mill and ultrasonic mixer) were used to prepare nanocomposite coatings. One percent (weight-based of wet film which would be 2% of dry film of coating since the coating has 50% solid content) of each of the three nanoparticles was added to the oil-based coating. One set was prepared using a high-speed mixer (Caframo overhead stirrers, BDC 3030) at 2000 rpm for 20 min. Later on during the project, another set was prepared in which nanoparticles were mixed with a high-speed mixer with a Cowles blade for 10 min at

2000 rpm, and then about 10% by weight glass beads (Zirconium beads of 0.8–1.0 mm) were added and samples were mixed for another 10 min using a Teflon blade (to minimize risk of breaking up the glass beads). Also, two sets were prepared using an ultrasonic mixer (Cole-Palmer ultrasound machine at 300 W) for 5 and 3 min, and the other one by a bead mill (Dyno-Mill, model 250-VSE-EXP from Eiger) for 10 min.

2.3. Investigating quality of dispersion

A number of coating properties were measured as indicators of nanoparticle dispersion. Viscosities of coatings (three nanocomposite coatings that were prepared using high speed mixer and glass beads and control) were measured using a Brookfield digital viscometer at 22 °C with spindle number 62. Uniform films of each coating were applied on the glass surfaces using a standard rod number 18 (48 μm wet film thickness) for a drying test. The drying times of samples were determined by BK-3 drying time recorder based on ASTM D5895 which was set for 24 h drying time.

A thin film (50 μm wet thickness) of each coating was applied on BYK Leneta (black and white) papers. After 24 h of air-drying: color, gloss and opacity of samples were measured using Minolta Spectrophotometer, BYK glossmeter, and X-rite spectrophotometer, respectively. ΔE color changes (CIE L^* a^* b^*) of samples were calculated based on ASTM D2244 and compared with the color of pure coatings (control without nanoparticles). The glosses of samples at 60° were measured on both black and white sections of coated Leneta charts. The opacity of each coating was compared with opacity of standard pure white paper. Glass transition temperature (T_g) of modified coatings with nanoparticles and pure coating were determined by differential scanning calorimeter DSC-Q1000. One-ml samples of each coating, cured on an aluminum plate at 60 °C for 24 h and left to air dry for two weeks were evaluated. T_g's of two replicate samples of each cured film were measured by DSC (Q500) at heating rate (ramp) of 10 °C/min, in a heat/cool/heat cycle from −40 °C to 350 °C.

The dispersion quality of nanoparticles into liquid coatings was measured by dynamic light scattering (DLS) technique at 25 °C with a Nano-ZS Malvern Zetasizer after 24 h of sample preparation. For DLS analysis the measured viscosities of coatings were used and the refractive index of linseed oil (RI = 1.47) [28] was considered as the main component of the coating.

Thin layers of each coating film were applied on small glass plates using a spin-coater (WS-650 MZ) at 2000 rpm. The quality of nanoparticle dispersion on the surfaces of dried films of coatings was measured by a number of surface analysis techniques. A set of gold coated samples was analyzed by scanning electron microscopy (Joel JSM-6610) in backscattered electron mode (SEM-BSC) at 15 kV. Also, pure nanoparticles and nanocomposite films were characterized by confocal laser scanning microscopy (CLSM) Leica DMR XE using 63× lens and numerical aperture (NA) = 1.4, in reflection mode of the green region (490–560 nm). A droplet of imaging oil (Leica type F immersion liquid) was added to the dry film on glass and a glass cover was placed on the top (to eliminate the effect of air bubbles). Dispersion of nanoparticles on the surface of carbon-coated samples was also examined by a field emission scanning electron microscopy (FE-SEM) using Hitachi S-5200 with 0.18 nm resolution at low accelerating voltage (1 kV).

Also, a set of samples that was mixed with high speed mixer, without glass beads initially, were used in ToF-SIMS analysis. A thin layer of each coating was applied on a silicone plate and dried in a dust free environment for one week. The high spectra mass resolution (spatial resolution of 1–3 μm) and high spatial resolution image (100–200 nm) of samples were collected on a ToF-SIMS IV (ION-TOF GmbH, Münster, Germany) equipped with a bismuth liquid Ion source. A Bi_3^{2+} primary ion beam (25 keV, 0.1 pA) was used