Nanoparticle Composites for Coating Applications

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ABSTRACT

Nanoparticles can be incorporated into polymeric coatings to enable significant improvement in targeted properties, i.e., scratch resistance, UV resistance, conductivity, etc. Commercial processing methods have been developed to surface treat nanoparticles to render compatibility between the nanoparticle and polymer matrix to control the average particle size and particle size distribution of the dispersed nanoparticles. In addition, commercial processes to disperse the surface treated nanoparticles have been developed. These integrated technologies allow transparent coatings containing nanoparticles to be formed in a wide range of resin formulations. This paper will address the preparation and analytical characterization of nanoparticle dispersions, as well as their performance attributes.

Keywords: nanoparticles, dispersion, coatings, transparency, scratch-resistant

1. INTRODUCTION

During the past several years, advances in nanomaterials have allowed them to be formulated into numerous applications. The majority of these applications sought performance improvements that were previously unobtainable. Examples of such applications containing nanomaterials that have been commercialized include scratch/abrasion resistant transparent coatings, sunscreen lotions to provide visible transparent UV protection, polishing slurries to provide pristine surfaces for optics, and environmental catalysts to reduce pollution.

The quest for improved scratch/abrasion resistant coatings is a goal for many coating formulators. Thousands of scratch resistant coating applications are present in our everyday lives. Examples of these applications include coatings for wood floors, safety glasses, electronic displays, automotive finishes, and polycarbonate panels. Improving the mar, scratch and/or abrasion in these transparent coating applications is a major challenge, particularly with regard to not affecting the other performance attributes of the coating.

Incorporation of inorganic fillers into coatings to improve mechanical properties is well known. Drawbacks associated with this approach can include loss of transparency, reduced coating flexibility, loss of impact resistance, increase in coating viscosity, and appearance of defects. To overcome these defects a filler material should impart improved scratch resistance without causing the aforementioned detriments. Nanomaterials have the potential to overcome many of these detriments because of their inherent small size and particle morphology.

Maintaining transparency in a coating containing inorganic filler particles is a challenge. Four properties dictate the degree of transparency in a composite material: Film thickness, filler concentration, filler particle size, and the difference in refractive index between the bulk coating and the filler particle. Mie theory describes the relationship between particle size, concentration, refractive index, and light scattering for spherical particles dispersed in a bulk phase as shown in equation 1.

$$I_s = (Nd^6/\lambda^4)\ \{[(n_p/n_c)^2-1]/[(n_p/n_c)^2+2]\}(I_i) \qquad (1)$$

I_s = Intensity of scattered light
N = Number of particles
d= Particle diameter
λ = Wavelength
n_p = Particle refractive index
n_c = Coating refractive index
I_i = Intensity of incident light

As is evident in equation 1, the magnitude of light scattering in a particle/coating composite is strongly influenced by the particle size. In addition, the greater the difference between the refractive indexes of the particle and that of the bulk coating, the greater the degree of light scattering.

Silica particles, colloidal or fumed, and clays are among the most widely studied inorganic fillers for improving the scratch/abrasion resistance of transparent coatings. These fillers are attractive from the standpoint that they do not adversely impact the transparency of coatings due to the fact that the refractive indices of these particles (fumed silica = 1.46, bentonite clay = 1.54) closely match those of most resin-based coatings. The drawback to silica-based fillers is that high concentrations of the particles are generally required to show a significant improvement in the scratch/abrasion resistance of a coating, and these high loadings can lead to various other formulation problems associated with viscosity, thixotropy, and film formation.

The use of alumina particles in transparent coatings is much more limited even though alumina is significantly harder than silica-based materials, and as a scratch and abrasion-resistant filler, higher performance at lower loadings is often observed. For alumina particle sizes greater than 100-nm, the high refractive index (1.72) results in significant light scattering and a hazy appearance in most clear coatings. Currently, only high refractive index coatings, such as the melamine-formaldehyde resins used in laminate production, can use submicron alumina for scratch resistance and maintain transparency.

2 NANOPARTICLE PRODUCTION

To use alumina as scratch-resistant filler in transparent coatings, the particle size must be sufficiently small to overcome its refractive index mismatch. Nanophase Technologies Corporation (NTC) has developed the Physical Vapor Synthesis (PVS) process that is capable of producing metal oxide nanoparticles via a bottoms-up method starting from metallic feed. This process allows production of nonporous crystalline metal oxides having primary particle sizes less than 100 nm at economically viable rates with essentially no byproducts or waste streams.

NTC produces two grades of aluminum oxide using the PVS process: NanoTek™ and NanoDur™ alumina. Both grades feature a mixture of γ and δ crystal phases and are spherical in shape, but the grades differ in terms of primary particle size. NanoTek™ alumina has a surface area of 35 m^2/g corresponding to a mean particle size of 48 nm, whereas NanoDur™ alumina has a surface area of 45 m^2/g with a mean particle size of 37 nm. A TEM image of NanoTek™ alumina is shown in Figure 1.

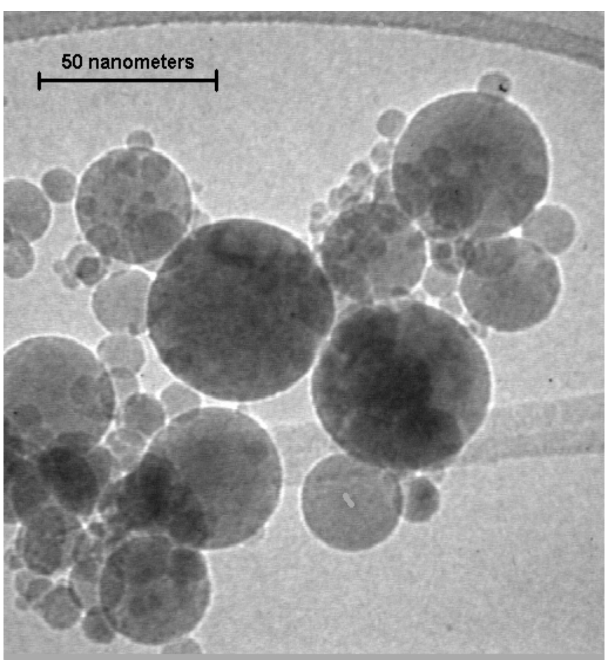

Figure 1: TEM image of NanoTek™ aluminum oxide

3. NANOPARTICLE DISPERSION

For nanoparticles to be of use in transparent coatings, it is critical that aggregates present in the powder be dispersible to their primary particle size in the coating formulation to avoid rapid settling and excessive light scattering. In addition, it is critical that the dispersed primary particles avoid re-aggregation during the coating curing process.

NTC has developed a proprietary particle dispersion-stabilization process that involves specific surface treatments designed to yield nanoparticles that are compatible with a variety of different coating formulations. For example, stable dispersions of metal oxide nanoparticles can be prepared in solvents such as water, alcohols, polar and nonpolar hydrocarbons, plasticizers, and even directly in acrylate monomers with the appropriate surface treatment process. These surface treatments allow solids levels of up to 60 wt% to be dispersed and yet maintain a sufficiently low viscosity for ease of blending.

The use of highly concentrated, non-aggregated, nano-particle dispersions allows incorporation of the nanoparticles into a coating formulation without substantial dilution of the formulation with the dispersion liquid. This feature is particularly important in 100% solids coating formulations wherein the nanoparticle is dispersed in one of the reactive monomers.

4. NANOPARTICLE COMPOSITES

Using concentrated dispersions of aluminum oxide nanoparticles in various solvents and reactive monomers, composites were prepared for a variety of transparent coating formulations including emulsion-based polyurethanes and polyacrylates, solvent-based two-component polyurethanes and melamine-polyols, and 100% solids UV-curable coatings. Importantly, the alumina nanoparticles also featured surface-treatments designed specifically for the formulation chemistry of the coating type in which it was dispersed.

Nanoparticle coating composites were prepared using both the NanoTek™ and NanoDur™ grades of aluminum oxide in a solvent-based transparent melamine-polyol coating to compare the haze of the two different particle sizes. The haze results are shown in Figure 2.

Three aspects of the haze data in Figure 2 are noteworthy. (1) As expected, the larger particle size NanoTek™ alumina (48 nm, mean) results in higher haze in the melamine-polyol nano-composite compared to those made with NanoDur™ alumina (37 nm, mean), at a given alumina loading level. (2) If transparency in a clear coating is defined as < 1% haze, it is apparent that the particle size of alumina used in the composite be no greater than 50 nm in order to maintain transparency. (3) Even with an alumina nanoparticle size grade of < 50 nm, improvement in scratch/abrasion resistance of the coating composite must be attainable with relatively low alumina loadings to stay within the transparency limit.

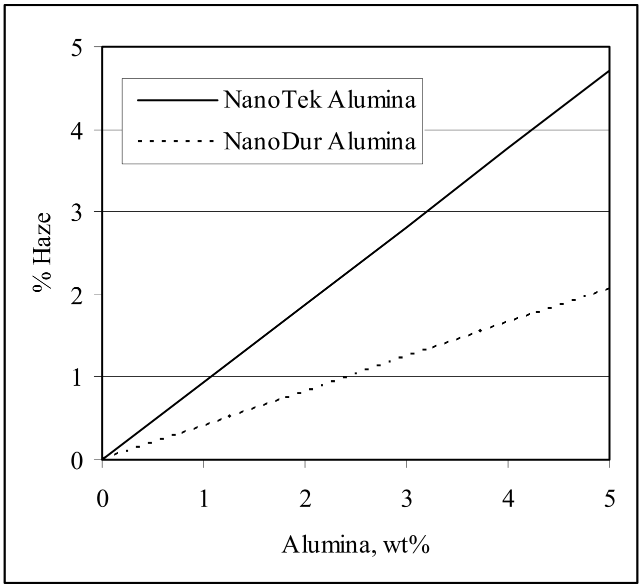

Figure 2: % Haze of alumina/melamine-polyol nano-composite coatings thermally cured to 1 mil thickness

Extension of the alumina particle size haze study to a variety of coating formulations with different refractive indices allowed the derivation of the empirical formula shown in equation 2 to predict the haze resulting from alumina incorporation in any nanocomposite coating.

$$\% \text{ Haze} = (8.8\text{x}10^{-6}\, d^3 - 1.4154\, n_c + 2.02)(\text{wt }\%)(\text{mil}) \quad (2)$$

d = Alumina particle diameter, nm
nc = Coating refractive index
wt % = Alumina loading level, wt % of total solids
mil = Cured coating thickness

5. SCRATCH-RESISTANT NANOCOMPOSITES

To evaluate the performance of alumina nanoparticles as a scratch-resistant filler in a transparent coating, a nano-composite was prepared with NanoDur™ alumina dispersed in a UV-curable coating formulation. The alumina nanoparticles were dispersed in 1,6-hexanedioldiacrylate, a reactive monomer, at 30 wt%, and this dispersion was blended with a UV-curable formulation to provide composite coatings with variable levels of alumina particles between 0.2 and 2.0 wt%. These composites were subjected to a scratch test involving 200 double rubs with a 0000 grade steel wool pad and the level of scratching quantified by measuring the increase in haze due to the scratches. The performance of the alumina-containing composite coatings was compared with the neat coating without alumina particles. The results of this scratch study are shown in Figure 3.

The performance of the alumina nanoparticles in Figure 3 is expressed as X times improvement in scratch resistance compared with the neat coating. It is evident the alumina nanoparticles significantly improve the performance of the UV-curable coating, up to a 9-fold improvement, even with very low levels of alumina incorporated in the composite.

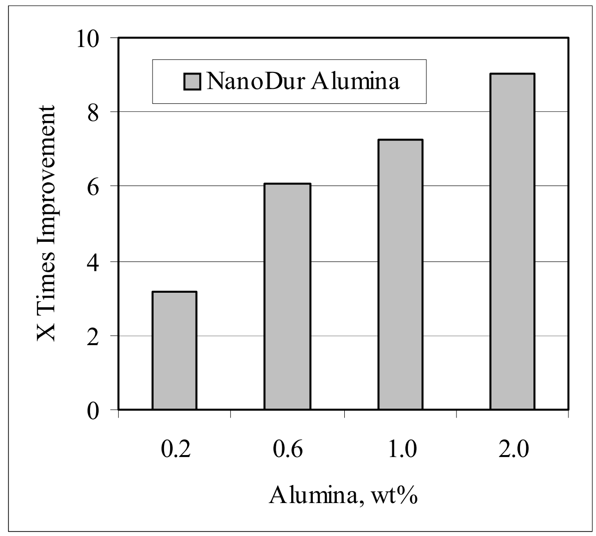

Figure 3: Scratch-resistance performance of NanoDur™ alumina particles in a UV-curable transparent coating

The scratch resistance properties of alumina nano-particles were also compared with silica particles at equivalent loading levels. The silica used in the study was the commercially available Nanocryl silica from Hanse Chemie. The silica particles are surface-treated and dispersed in 1,6-hexanedioldiacrylate and were blended into the same UV-curable coating formulation as the alumina particles. The comparative performance is shown in Figure 4.

As is evident in Figure 4, the alumina particles provide much better scratch resistance protection for the UV-curable coating compared to the silica particles at equivalent particle loadings. The much harder alumina particles are superior at preventing steel wool scratching compared to the softer silica particles.

The scratch resistance performance of alumina nano-particles incorporated into a variety of other transparent coating compositions was also evaluated. A level of 1 wt% alumina particles was used in all cases, and the alumina particles were introduced in the coating formulations by dispersing the alumina at high concentration into the appropriate solvent used in the coating formulation, then blending into the formulation at a level to yield 1 wt% particles with respect to the total solids in the cured coating.

The scratch resistance performance was measured using the same steel wool scratch test as was applied to the UV-curable coatings. The results of this study are summarized in Figure 5.

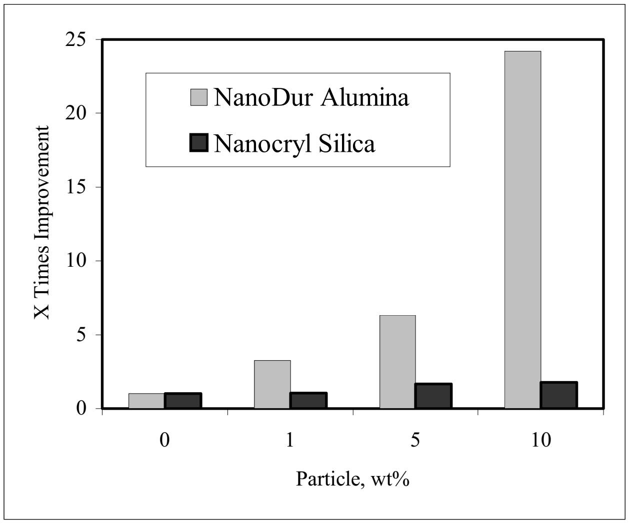

Figure 4: Comparison of the scratch-resistance performance of NanoDur™ alumina particles and Nanocryl™ silica particles in a UV-curable transparent coating

Several features can be noted by comparing the relative alumina performance in different transparent coating formulations in Figure 5. First, there is a range of scratch improvement dependent upon the particular formulation within the coating class. For example, the scratch resistance UV-curable coatings can be improved anywhere from 5 to 10 fold with the incorporation of 1 wt% alumina, depending on the type and concentration of reactive acrylate components used in the formulation. Performance ranges for the melamine-based coatings, 2K polyurethane coatings, and emulsion-based coatings evaluated were also observed.

Within a given coating class, those formulations that resulted in harder/stiffer coatings tended to show greater improvement with alumina incorporation than did those formulations that lead to softer/more thermoformable coatings.

In addition, those transparent coating formulations which exhibit cross-linking upon curing, such as UV-curable, 2K polyurethane, and melamine-based coatings, showed greater improvement in their scratch-resistance upon alumina nanoparticle incorporation compared to transparent coatings which do not cross-link but rather coalesce, such as emulsion-based coatings.

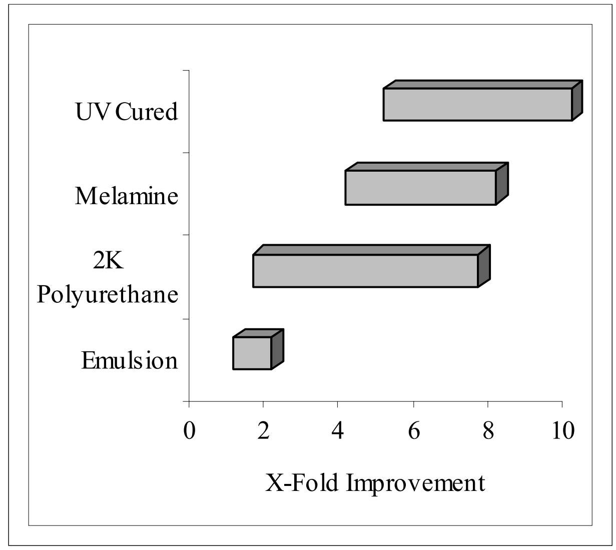

Figure 5: Scratch-resistance performance of NanoDur™ alumina particles at 1 wt% loading in various transparent coating formulations