High Performance UV Curable Organic-Inorganic Hybrid Coatings for Plastics

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Introduction:

Thermal plastics have been used widely in applications such as consumer electronics, appliances, optical lenses, glazing, and automotive parts. They offer many advantages over metal, glass or ceramic materials, including light weight, high impact strength, ease of processing, and versatile styling capability. However, poor scratch resistance and chemical resistance are major drawbacks for thermal plastic substrates in some applications. Many clearcoat technologies have been developed for plastics to improve scratch/abrasion resistance and chemical resistance.[1, 2, 3] UV curable options based on acrylates have been widely adopted by the manufacturing industry due to their high production efficiency, low volatile organic content (VOC) and reduced energy consumptions.

More recently, nanoparticle/acrylate monomer dispersions have been made commercially available,[4,5] and this provides a practical route to prepare UV curable organic-inorganic hybrid aiming for higher level of abrasion resistance than organic coatings. In this paper, we present a UV curable organic-inorganic nanohybrid clearcoat system developed based on inorganic nanoparticle dispersions. With its ceramic-like features, the coating exhibits exceptional clarity and scratch resistance, and offers eco- and user-friendly attributes provided by UV curing technology. The effects of nanoparticle content, particle size and dispersing matrices, and application conditions such as film thickness and curing energies on coatings physical performance, especially abrasion resistance, are studied and discussed.

Experimental:

- All raw materials were used as received.
- Combinations of mono and multifunctional acrylates were used and required no further modification.
- Inorganic nanoparticles used are commercially available.
- Photoinitiators are commercially available.
- Substrate: Mokrolon® clear polycarbonate (Bayer AG).
- Formulas were adjusted to 60% solids for spin application.

Application:

Polycarbonate plaques were wiped with 2-propanol and air dried. Coating solutions were spin-applied and flashed under ambient conditions for 5-10 minutes. The coatings were then cured with a Fusion unit, equipped with H bulbs under air atmosphere. The conveyer speed and lamp height were adjusted to provide UVA dosage of 0.5-1 J/cm^2 and intensity of 0.5-0.6 W/cm^2.

Tests:

- Adhesion: Crosshatch/tape pull test, using Nichibon LP-24 adhesive tape. Rating scale 0-5 referring to no adhesion to 100% adhesion after tape pull.
- Optical clarity: Haze% was measured with Hunter Lab spectrophotometer. Results were reported as average of 4 readings from different locations on each sample.
- Abrasion resistance: Taber 5150 Abrader (Taber Industries), CS-10 wheels, 500 grams of weight. Haze% was measured after 100 or 300 taber cycles.
- Chemical resistance: Approximately 1 ml of each testing chemical was applied on coating surface and then covered with watching glass. After 24 hours, testing spot was wiped and coating appearance was visually evaluated (no change – good). Tested chemicals included acetone, isopropyl alcohol, concentrated ammonia, yellow mustard, vegetable oil, mayonnaise, suntan lotion, brass polish, and lipstick.
- Microscopy: Field Emission Scanning Electron Microscopy (Carl Zeiss/LEO 1530 FE), operated at 5 kV accelerating voltage.

Results and Discussions:

Organic-inorganic nanohybrid coatings were formulated by incorporating different types of inorganic nanoparticle/acrylate dispersions into a control acrylate mixture (coating 1). An industry state-of-the-art organic UV curable abrasion resistant clearcoat (coating 2) was included for comparison. All coatings were spin-applied with a dry film thickness of 12-15μm. Taber abrasion resistance was compared by measuring haze% developed after 100 and 300 taber testing cycles respectively. The results are summarized in Table 1. All formulas with nanoparticles showed remarkable improvements in abrasion resistance, exhibiting much lower haze after a 100 cycle taber test than the control. When compared to the state-of-the-art organic UV abrasion resistance clearcoat, more significant improvements were observed under more aggressive tests at 300 cycles, indicating a better performance for long term endurance. It was noticed that some of hybrid formulae exhibited high initial haze, possibly due to larger particle size or incompatibility of the nanoparticle dispersion with rest of the formula components. When selecting proper inorganic dispersions for coating formulations with high clarity requirements, these characteristics need to be further considered.

Table 1. Hybrid coatings formulated with different nanoparticle acrylate dispersions.

Coating	1	2	3	4	5	6	7	8	9
Nanoparticle acrylate dispersion	n/a	n/a	#1	#2	#3	#4	#5	#6	#7
Inorganic wt%	0	0	20	25	25	25	25	25	25
Initial Haze%	0.5	0.5	1.8	3.9	2.9	3.9	2.7	0.7	4.7
Haze% after 100 taber cycles	39.0	25.8	20.8	20.2	20.0	16.7	17.4	13.5	15.7
Haze% after 300 taber cycles	n/a	49.9	24.3	25.4	28.6	24.0	25.8	19.7	23.8

To study the effect of inorganic content on abrasion resistance, a series of hybrid coatings were prepared with one type of nanoparticle acrylate dispersion (#6) with a nanoparticle content varying from 8 to 35%. The coatings were applied with 12-15μm final dry film thickness. Again, taber abrasion resistance was evaluated at 100 and 300 cycles. As shown in Table 2, 100 cycles taber abrasion resistance was substantially improved when incorporating even a low level of 8% of nanoparticle. When the inorganic level was increased to 25%, performance at 300 taber cycles was significantly enhanced. Within the tested range, coatings with higher nanoparticle content showed overall higher abrasion resistance. Since all coatings demonstrated excellent adhesion over polycarbonate substrate, the improvement on abrasion resistance is considered to be attributed, to a great extent, to the presence of inorganic particles. However, yet not observed from this study, it is possible that if inorganic content is too high, the coating matrix may become too rigid with reduced capability of dissipating the stress during the abrasion process, resulting low abrasion resistance.

In this study, each coating was cured with 2 levels of UV dosage. Comparable abrasion resistance was obtained with coatings cured with a dosage of 1J/cm^2 and with reduced dosage of 0.5J/cm^2. In fact, coatings with a high level of inorganic nanoparticle content trend towards less performance difference when cured with varied UV energy, indicating a wider curing window for application. This could be attributed to the fact that higher inorganic content requires less total energy for curing since there is relatively less amount of monomer per unit coating volume.

Table 2. Hybrid coatings formulated with varied levels of inorganic nanoparticle[1] and cured with different levels of UV energy.

Coating	1	10	11	12	13	14	15	16	17
Inorganic (wt%)	0	8	8	15	15	25	25	35	35
UVA (J/cm^2)	1	0.5	1	0.5	1	0.5	1	0.5	1
Adhesion	5	5	5	5	5	5	5	5	5
Haze% after 100 taber cycles	39.0	15.7	10.7	11.3	11.9	10.1	8.8	10.1	7.6
Haze% after 300 taber cycles	n/a	42.8	39.5	33.4	39.5	19.4	19.7	14.9	15.9

1. #6 nanoparticle dispersion.

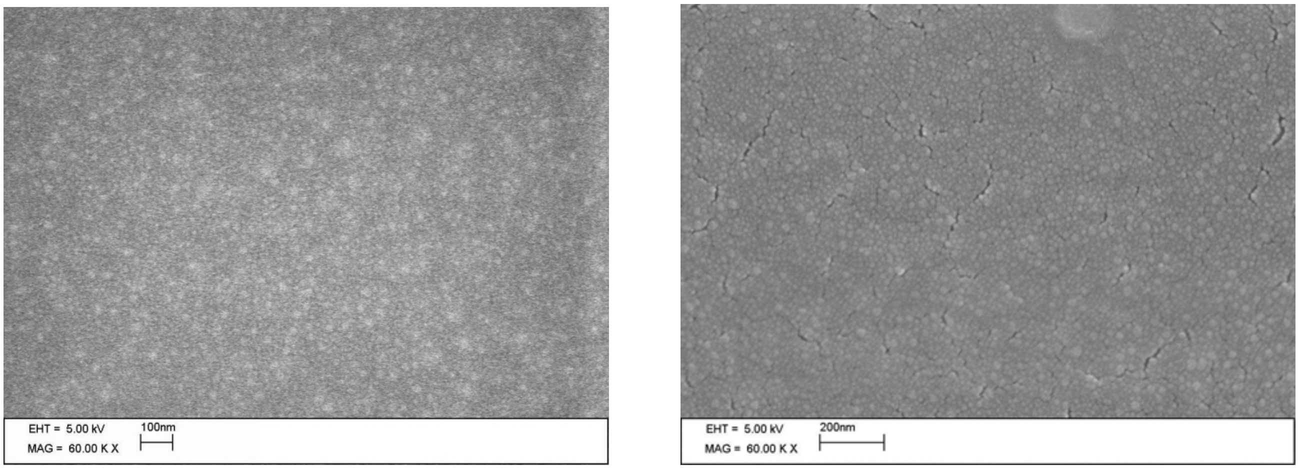
For many abrasion resistant clearcoat applications, thin film coatings are of special interest due to, among other attributes, excellent optical and cosmetic performance and great cost effectiveness. To study the hybrid coating performance over the low film thickness range, samples were prepared with the same coating (coating 15) at different film thicknesses ranging from 3 to 18μm. As shown in Table 3, all coating thicknesses exhibited excellent optical clarity with low initial haze. More importantly, consistent abrasion and chemical resistance were observed at all film thickness, indicating a strong potential for using the hybrid system in low film thickness coating applications.

Table 3. Performance of hybrid coating with 25% of nanoparticle[1] with varied film thickness.

Testing	Results				
Film thickness (μm)	3	5	8	12	18
Adhesion	5	5	5	5	5
Initial haze%	0.1	0.1	0.1	0.1	0.2
Haze% after 100 cycles of taber abrasion	9.4	10.1	10.2	7.9	10.0
Haze% after 300 cycles of taber abrasion	10.8	13.0	13.0	11.3	11.0
Chemical resistance	Good	Good	good	good	good

1. #6 nanoparticle dispersion.

To better understand the organic-inorganic hybrid structure, coating morphology and particle distribution were studied with a Field Emission Scanning Electron Microscopy (FESEM). The top surface views of the coating containing 25% of inorganic particles showed in Figure 1 includes micrographs of the “as received” surface (a), and the surface after 30 seconds of plasma ashing to remove top-layer organic content for a more distinctive image of inorganic particles (b). These images clearly reveal the presence of a layer of nanoparticles uniformly dispersed on the surface of hybrid coating with no particle aggregation and large scale organic-inorganic phase separation. A sectional FESEM micrograph of the coating in Figure 2 shows that inorganic nanoparticles are evenly dispersed throughout the entire coating layer. Such a 3-dimensionally homogeneous inorganic nanoparticle dispersion structure explains the ceramic-like abrasion resistance, as well as the high optical clarity.



(a) (b)

Figure 1. Representative surface FESEM micrographs of hybrid coating. (a) before ashing, (b) after ashing at 60,000X magnification.

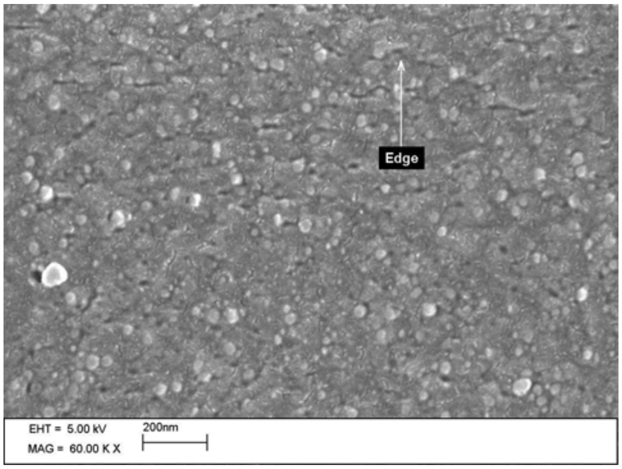


Figure 2. Representative cross sectional FESEM micrographs of hybrid coating at 60,000X magnification.

Conclusions:

The appropriate addition of inorganic nanoparticles provides greatly enhanced abrasion resistance and chemical resistance, and as the inorganic content increases, the hybrid system exhibits exceptional ceramic-like abrasion resistance while maintaining excellent adhesion to plastic substrates. Due to the small particle size and homogenous particle dispersion, the coatings exhibit excellent optical clarity. These coatings also provide user-friendly features by demonstrating almost identical performance properties when cured at varied energy range and film thickness, under ambient air atmospheres. Furthermore, the introduction of inorganic nanoparticles provides improved eco-friendliness due to lowered usage of petroleum based chemicals in coating products. Potential applications of these high-performance hybrid coatings include a variety of commercial products such as consumer electronics, appliances, automotive parts, and optical lenses.

Acknowledgments:

The authors would like to thank Fred A. Stewart-Davis from PPG Industries, Inc. for conducting FESEM analyses.

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