Performance Optimization of UV Powder Coatings by Combining Resin Systems

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1. Introduction

UV (ultraviolet) radiation cured powder coating is a technology that combines the advantages of thermoset powder and liquid UV curable coatings. Unlike thermoset powder coatings, UV curable powder coatings separate the processes of melting and flow-out from actual curing during UV radiation. More precisely, when exposed to heat, UV curable powder coating particles melt and flow into a homogeneous film that is crosslinked only when it is exposed to UV light.

Typically, the crosslinking mechanism employed in UV curable powder coatings is a free radical process. During UV irradiation, photo initiators are activated in the molten film resulting in the formation of free radicals. These free radicals then further react with available unsaturation promoting polymerization (crosslinking) of the powder coating.

Final coating appearance and properties depend on resin selection, photo initiators, pigments, fillers, additives, powder coating processing conditions, and curing parameters .Variability of the crosslinking efficiency of specific formulations and cure conditions can be assessed by using differential photocalorimetry.(1)

Recent improvements in UV powder coating technology have produced systems that exhibit very high flow making smooth finishes achievable at temperatures as low as 100°C.(2) Technological improvements and economic benefits have propelled a growing interest in the UV powder coatings as illustrated by the data in Figure 1 showing a sharp increase in the number of UV curable powder patents over the last thirty years.

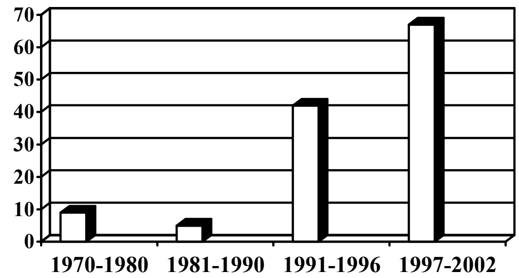

Figure 1 *– Global Patents on UV powders over years*

The years 1996, 1997 and 1998 were extremely active with regards to UV powder technology patent applications. Note that the "pioneers" in the UV powder systems were already active in 1970.

Many solid resin systems are now commercially available for use in UV powders cured by a free-radical polymerization. These include acrylated or methacrylated polyesters or polyacrylates(3), fumaric acid-based polyesters alone(4) or in combination with solid vinyl ethers(5), acrylated or methacrylated epoxy resins(6) and acrylated urethane based systems.(7) Solid grade epoxy resins that are UV cured via a photocationic mechanism(8) are also available.

2. Polyester / Epoxy Combined Chemistries in UV Powder Coatings

Film performance requirements for markets utilizing substrates such as wood, wood composites, plastic, and metal can be achieved by combining solid-grade UV curable polyester and epoxy chemistries developed for powder coatings. Although "hybrid" powder systems (carboxyl functional polyester with epoxy resins) have been known for more than thirty years in thermoset powder coating, low temperature cure (e.g. 120°C or less) can be problematic requiring long cure times to produce minimal properties. By contrast, "hybrid" UV cured powder coating films can achieve full properties in a short time (e.g. 1-3 minutes) when exposed to low temperature heat followed by UV light irradiation.(9)

"Hybrid" UV curable powder coatings (methacrylated polyester with acrylated epoxy resins) exhibit an interesting blend of properties when cured. For example, inclusion of a polyester backbone can improve light (yellowing) resistance of the coating when subjected to weathering tests while inclusion of an epoxy backbone gives outstanding chemical resistance, improved adhesion, and overall smoothness.

Manufacture of a “hybrid” polyester/epoxy blend can be done in 4 steps -

Formation of the UV curable polyester component –

1. Polycondensation in the melt of a phthalic dicarboxylic acid derivative (PA) with a glycol such as neopentylglycol (NPG) at 240°C in the presence of an esterification catalyst such as butyl stannoic acid produces a carboxy-terminated polyester.
2. Addition of glycidylmethacrylate (GMA) to the molten carboxy -terminated polyester while maintaining temperature at 200°C or less terminally grafts any methacrylate groups to the polyester chains through an addition reaction. Note that toxicological considerations have eliminated the use of *glycidylacrylate*. Also, inhibitors must be used to prevent gelation.[(2)]

Formation of the UV curable epoxy component –

3. Addition of acrylic acid (AA) to a molten diepoxy resin produces an epoxy diacrylate polymer.

Combining the two components -

4. The methacrylated polyester and the acrylated epoxy resin are homogeneously blended by extrusion to produce the final 2 resin system.

The following variables have been investigated to optimize properties of “hybrid” (polyester/epoxy) UV curable resin systems -

1. Selection of the aromatic di-acid (PA) between phthalic- , terephthalic- or isophthalic acid.
2. Partial substitution of the selected aromatic di-acid (PA) by an aliphatic di-acid like adipic acid or 1, 4-cyclohexanedicarboxylic acid.
3. Partial substitution of NPG by other glycols such as 1, 2-ethyleneglycol or 1, 6-hexanediol or 1, 4-cyclohexanedimethanol.
4. Branching of the polyester chains by incorporating polyfunctional monomers like trimethylolethane or trimellitic acid. The weight% of the chosen branching unit was determined using Flory’s equation to avoid polyester gelation during synthesis.[(10)]

Table 1 compares properties of a methacrylated polyester resin to two blends of the polyester with an acrylated type 3 epoxy resin based on bisphenol A and epichlorohydrin.[(11)]

Property	Methacrylated polyester	Methacrylated polyester / acrylated epoxy - blend 1	Methacrylated polyester / acrylated epoxy - blend 2
Double bond equivalent weight (g)	1500	1300	1100
Glass transition Tg (°C)	57	53	52
Brookfield viscosity at 200°C (mPa.sec.)	5500	2500	1950

Table 1 *- Characteristics of polyester / epoxy blends for UV powders*

Blending of the polyester and epoxy components produces distinct differences in melt viscosity, Tg, and unsaturation. Blend 2 exhibits the lowers viscosity which translates into the highest flow (smoothness) but the Tg of Blend 2 is essentially unaffected (as compared to Blend 1) insuring adequate storage and handling of powder paints.

3. UV Curing of Powder Coatings on MDF

For testing purposes, blends of methacrylated polyester and acrylated epoxy resins were formulated into a UV curable powder coating (Table 2) and cured utilizing the profile shown in Figure 2. The substrate under study was MDF (medium density fiber board).

Product	Weight (g)
(meth)acrylated resins	750
Hydroxyketone photoinitiator	10
Acylphosphine – oxide photoinitiator	10
Titanium dioxide	250
Wax	30
Flow agent	10

Table 2 *- UV curable powder coating formulation for testing*

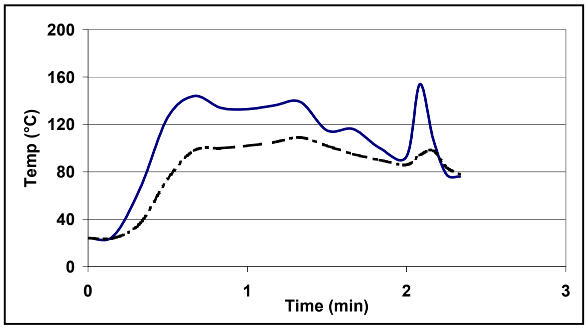

Figure 2 *- Heating / curing profile applied on MDF*
(Solid line = surface temperature)
(Broken line = temperature beneath the surface)

Initially, medium infrared radiation was applied to melt the powder particles. Once melted, the coated substrate was passed through a second zone using convection heat to maximize smoothness. Finally, the coated substrate was subject to UV irradiation to complete the cure (crosslinking). Note that UV irradiation always increases the <u>surface</u> temperature of the film but measurements clearly show that the temperatures immediately beneath the film surface are well controlled and limited to a maximum of 110°C for the entire cycle of approximately 3 minutes. This cycle time is very short when compared to those required for thermoset powder coatings curing at about 140°C.

The enhanced reactivity of "hybrid" (polyester / epoxy) UV curable powder coatings is shown in *Table 3*. A dosage of 3000 mJ/cm2 is required to cure the single component polyester coating while only 1500 mJ/cm2 is required to complete the "hybrid" cure. Completeness of cure was determined by a MEK rub test (methylethylketone).

UV-V dose (mJ/cm^2)	**Methacrylated polyester Powder**	**Methacrylated polyester/acrylated epoxy powder – blend 2**
1500	50	> 200
3000	> 200	> 200

Table 3 *- MEK rubs of UV cured polyester / epoxy blends*

4. <u>Optimization of Glass Transition Temperature (Tg) and Melt Viscosity</u>

The choice of phthalic acid derivative (PA) used in two methacrylated polyesters produced resins with similar glass transition temperatures (Tg) but with very different melt viscosities. Polyesters having a high Tg and a low melt viscosity produced a binder with the lowest melt viscosity and there by the highest level of film smoothness when blended with acrylated epoxy resins. (*Table 4*)

Property	**Methacrylated polyester A**	**Methacrylated polyester B**	**Blend methacrylated polyester A / acrylated epoxy**
Tg (°C)	54	55	50
Brookfield melt viscosity at 200° C (mPa.sec)	1600	5500	1000

***Table 4** - Comparison of Tg and viscosity between various resins and blends for UV powders*

Five variations (see below) were studied to determine the *lowest* melt viscosity for a binder containing methacrylated polyester A and an acrylated epoxy resin. Modifications were -

Mod 1 - Type and weight% of the polyester branching unit.

Mod 2 - Partial substitution of the phthalic acid derivative (PA) by adipic acid - a long chain aliphatic dicarboxylic acid.

Mod 3 - Partial substitution of neopentylglycol (NPG) by 1, 6-hexanediol - a long chain aliphatic diol.

Mod 4 - Substitution of the type 3 epoxy resin by a type 2 epoxy resin also based on bisphenol - A and epichlorohydrin.

Mod 5 - Substitution of the aromatic epoxy resin by an aliphatic epoxy resin based on hydrogenated bisphenol – A.

Tg and Brookfield viscosity measurements are shown in table 5.

Property	**Mod 1**	**Mod 2**	**Mod 3**	**Mod 4**	**Mod 5**
Tg (°C)	45	45	44	42	41
Brookfield viscosity at 175°C (mPa.sec.)	2000	2500	2900	1700	990

***Table 5** - Effect of structure modifications on Tg and viscosity of methacrylated polyesters*

As shown in Table 5, modifications 4 and 5 reduced Tg to an unacceptable level. Also note that the addition of hydroxyketone photoinitiators to a binder will lower Tg by approximately 2°*C/weight%* added[12]. "Hybrid" UV curable powder coatings based on polyester/epoxy combinations produce extrudates that can be difficult to grind. Additionally, some caking of the powder coating can occur during storage as well as impact fusion during application. Nevertheless, these limitations can be controlled by air conditioning (storage and dose air), using water cooled grinders, etc.

5. Case Studies Illustrating Optimal Performance Due to Combined Chemistries

5.1 . UV Powders for smooth matte finishes

The development of *smooth matte* finishes for metal and MDF applications was made possible by the development of "hybrid" UV powder systems. Smooth matte clearcoats have been successfully applied to hardwood and veneered composite boards (beech, ash, and oak) and to PVC used to manufacture resilient flooring where the presence of the epoxy resin in the binder increased chemical resistance of the coating to an acceptable level.

5.2 . UV Powders for wooden furniture

"Hybrid" UV curable powder coatings pass DIN 68861 specifications that includes specific requirements for chemical, abrasion, scratch, and heat resistances when applied to MDF (Medium Density Fiberboard), The results of DIN 68861 testing has described in detail in 4 recently published papers.[9,13,14,15] Summarizing those results - varying the polyester / epoxy ratio changes accelerated weathering tests (yellowing) results – that is, as the amount of polyester resin in the binder is increased, yellowing of the coating due to light exposure is reduced. To meet all requirements in DIN 68861, a compromise between UV resistance (yellowing), chemical resistance, and smoothness needs to be found.

5.3. UV powders with improved adhesion for metal

"Hybrid" UV curable powder coatings applied to metallic substrates show excellent adhesion and thus improved corrosion resistance. Copper Accelerated Salt Spray (CASS) testing as dictated by ASTM B368 has been used to determine the corrosion resistance of clear and white formulations applied to yellow chromated aluminum and electrolytic chromium coated steel.[1]

5.4. Clearcoats on plastics

When applied as protective clearcoats on PVC tiles used to manufacture resilient flooring or on Sheet Molding Compound (SMC) panels for OEM applications, UV curable blends of polyester and epoxy resins produce films with high levels of flexibility and chemical resistance.[13] A third requirement needed for flooring applications is good abrasion resistance. Currently, only matte clearcoats will meet the abrasion resistance requirement. Work is underway to produce a UV curable high gloss clearcoats with similar properties.

5.5 UV curable toners

Laboratory studies have determined that UV curable (meth)acrylated polyester / epoxy blends can produce binders suitable for colored toners.

6. Conclusions

Combining polyester and epoxy chemistries into "hybrid" UV curable powder coatings produces films that are very smooth, exhibit good adhesion and chemical resistance when applied to wooden furniture, metal, or plastic substrates. Additionally, these binders have been found to be acceptable for toner applications. Using structure modifications studies, the best combination of low melt viscosity and acceptable Tg values (above 45°C) has been determined. All 'hybrid" UV curable powder systems have been based on a blend of a methacrylated polyester and an acrylated bisphenol A epoxy resin.

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