Cure Behavior of Polyester-Acrylate Hybrid Powder Coatings

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INTRODUCTION

Increasingly stringent health, safety, and environmental regulations within the industrial finishing industry have caused coatings formulators to focus on the development of technologies that meet the dual requirements of environmental compliance and high performance. As a result, powder coatings are enjoying high growth as industrial finishers look for ways to meet these challenges. Carboxylic acid functional polyester resins for powder coatings in particular have experienced increased acceptance in the marketplace. Their ability to be cured by a wide range of epoxide curatives illustrates the versatility of this technology.

Triglycidyl isocyanurate (TGIC) is commonly used to cure these polyesters. Since the early 1980s, TGIC-cured polyester powder coatings have been very successful in gaining market share, particularly in applications requiring excellent exterior durability, such as automotive trim, patio furniture, and lawn and garden equipment. From 1985 to 1995, U.S. thermosetting powder coatings market share of polyester TGIC powder coatings increased from approximately 11 to 19.5%.1,2

Legislation recently passed by the Technical Progress Committee of the European Commission indicates that powders containing TGIC have to be labeled according to the provisions of the Hazardous Materials Directive.3 Table 1 illustrates a few curing agent alternatives that have been introduced in the marketplace in attempts to address this issue.

Acrylate-Cured Polyester Powder Coatings

Glycidyl methacrylate (GMA) acrylic resins provide the polymeric backbone to powder coatings now being evaluated for the future topcoat/clearcoat of automobiles.4 These resins have excellent resistance to environmental hazards such as ultraviolet light and acid rain. Also, because of its highly polar nature, polymers based on GMA have excellent adhesion to metal substrates.5 Therefore, they have been chosen as candidates for use as crosslinkers in polyester powder coatings requiring high durability.

Volatile-free, two-component powder coatings have recently been developed that offer the performance properties of TGIC-cured polyester coatings.6 These curing systems are based on epoxide-functional acrylate resins, utilizing GMA.

Development of a polyester/acylate curing system necessitates the optimization of both the polyester and acrylate resins. As is typical in powder coatings, an imbalance or weakness in one of the binder components' properties usually will detrimentally affect the entire coating system. For example, if either component has a glass transition temperature (Tg) below 40°C, the storage stability of the powder paint will usually be poor.

A balance of appropriate coating viscosity during the curing process (chemorheology) and reactivity is necessary to produce a highly crosslinked film with adequate open time to flow, the result being a smooth visual appearance with good mechanical and chemical properties. Comparison of the melt viscosity behavior of the polyester/acylate system and other common commercial powder coatings (Figure 1), indicates that the rate of viscosity increase occurs more rapidly in the polyester/acylate system.
Table 1—TGIC-Free Alternatives

<table>
<thead>
<tr>
<th>Current Alternatives</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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<tbody>
<tr>
<td>1:1 Hydroxyalkyl amide (HAAAM)</td>
<td>Good mechanicals</td>
<td>Volatilities, yellowing,</td>
</tr>
<tr>
<td>(TMMGU)</td>
<td>Low toxicity</td>
<td>hydrolytic stability-clouds</td>
</tr>
<tr>
<td>Tetramethoxymethylglycoluril</td>
<td>Good mechanicals</td>
<td>Volatilities, storage stability</td>
</tr>
<tr>
<td></td>
<td>(TMGCU)</td>
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EXPERIMENTAL

Powder Coating Formulation and Processing

White powder coatings were formulated on a 1:1 epoxide:acid equivalence basis, using a 0.5/1.0 pigment/binder ratio. The general formulation is shown in Table 2.

Premixing of each formulation was performed in a Henschel FM-10 high-intensity mixer for two minutes. Extrusion was carried out with a Werner & Pfleiderer ZSK-30 twin screw extruder operated at 250 rpm, with Zone 1 set @ 100°C, and Zone 2 set @ 80°C. The molten extrudate was cooled by means of Strand chill roll. The resulting chips were ground with a Brinkmann ZM-1 centrifugal mill at 15,000 rpm. Powder was classified with a 200 mesh sieve, utilizing a Powder Process System reverse air sieve, and applied electrostatically onto cold-rolled steel panels with a Nordson Versa-Spray corona charging gun. The applied voltage was 80 kV. Film thickness of the coated panels ranged from 50-63 μm, and the cure schedule for each coating was 15 min at 200°C.

Coating Characterization Methods

GEL TIME REACTIVITY TEST (Powder Coating Institute (PCI) Recommended Procedure #6, Powder Coating Institute Test Method Manual, Powder Coating Institute, 1800 Diagonal Road, Suite 370, Alexandria, VA 22314): A Thermoelectric Co. cure plate, set at 200°C, was utilized for measuring each powder coating's gel time.

INCLINED PLATE FLOW (PCI Recommended Procedure #7): Powder pellets were made using a Parr pellet press and the pellets were placed on 25 mm × 75 mm × 1 mm microscope slides. The slides were then transferred to a 62.5° angled steel plate maintained at 180°C. After a 15-min contact time, the distance of pellet flow was recorded.

GEL FRACTION ANALYSIS: Powder coatings were electrostatically applied to aluminum plates, each plate containing a release agent. After curing the powders at 200°C for 10 min, the films were removed from the aluminum substrate and weighed on a Mettler AE-200 analytical scale, then dipped in acetone for 24 hr. The specimens were then allowed to dry for one hour in a 100°C oven and weighed again. The fraction of film retained by weight was recorded.

MELT VISCOMETRY (ASTM D 4287-88): The melt viscosity of each resin was measured with an ICI Cone & Plate Viscometer, Model VR-4510 (BYK-Gardner, Inc.) using a VR-4200 cone with a cone angle of 2°C and a nominal diameter of 0.56 in. The shear rate was 3,600 second⁻¹.

DIFFERENTIAL SCANNING CALORIMETRY (DSC): The samples were sealed in hermetic aluminum pans and scanned with the TA Instruments DSC 2920 by heating from 0° to 280°C at 10°C/min. The glass transition and fusion (Tg) temperatures were determined from the midpoint of the respective endothermic transitions. The onset of the cure temperature (Tc) was determined from the cure exotherm transition. The Arrhenius parameters, pre-exponential factor (log(Z)), and activation energy (Ea) as well as the heat of reaction (AH) were calculated using the Borchardt and Daniels Kinetics Data Analysis Program, version 4.0.

CHEMORHEOLOGY: The flow and cure properties of the powder coatings were recorded on a TA Instruments CSR 2500 Stress Rheometer equipped with an EMT high temperature unit. The CSR 2500 was operated at 1% strain for all samples using a parallel plate geometry with a 0.5 mm gap. The temperature was ramped from 30° to 250°C at 5°C/min heating rate for all samples, and the frequency of the experiments was set at 1.0 Hz. Stress sweep measurements showed no signs of non-linearity under these conditions.

A sequence of tests was also performed to simulate a practical oven cure schedule of 10 min at 180°C. This was carried out by heating each sample from 30° to 180°C at a rate of 30°/min. The samples were then held at this peak temperature for an additional five minutes. The frequency and strain were set at 1.0 Hz and one percent, respectively.

By applying a defined stress and measuring the magnitude and phase angle of the resulting displacement, the complex modulus (G*) can be determined. From this parameter, the complex viscosity (η*) and storage modulus (G′) were calculated. The Arrhenius kinetic crosslinking parameters, log(k∞) and Eν, were determined.

![Figure 1—Melt behavior of common powder coatings.](image-url)