AAN024

DMA to improve Powder Coatings*

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BACKGROUND

Powder coating is an advanced method of applying a decorative and protective finish to a wide range of materials and products that are used by both industries and consumers. The powder used for the process is a mixture of finely ground particles of pigment and resin, which is sprayed onto a surface to be coated. The charged powder particles adhere to the electrically grounded surfaces until heated and fused into a smooth coating in a curing oven.

Today, powder coatings are primarily being used in home appliances, automotive, building, oil and gas piping, machinery, outdoor products and also non-metal products. Powder coating is the fastest-growing finishing technology, representing over 10% of all industrial finishing applications. The global powder coating market was estimated to 70.6 billion US$ in 2000.

Resins used in powder coatings may be either thermoplastic (flows when heat is applied) or thermosetting (cross-links when enough heat is applied). Typical thermoplastic powder coatings include: polyethylene, polypropylene, nylon, vinyl, polyvinyl chloride, polyvinylidene fluoride, thermoplastic polyamides, and thermoplastic polyesters. These are high-molecular-weight polymers that exhibit excellent chemical resistance, toughness, and flexibility. They are difficult to grind into fine particles, and have a high viscosity when heated. Thermoplastic powders are especially well suited for a thick coating capable of extreme performance requirements

Thermosetting powders are derived from three generic types of resins: epoxy, polyester, and acrylic. From these three resins, five coating systems are derived: epoxy, epoxy-polyester, polyester-triglycidyl isocyanurate, acrylic-urethane, and polyester-urethane.

The powder coating formulation is much like a liquid coating formulation except that most of the components are in solid, melt processable form. The main components of a thermosetting powder coating are: - **Resin,** the key component of powder coatings; **Curing agents**, depending on the type of resin system employed and the final coating properties required; **Accelerators** to increase the cure reaction rate; **Pigments**; **Fillers** to reduce the cost of the coating formulation; **Degassing agents** to improve out-gassing and eliminate pinholes and craters; **Dry Flow agents** to improve the free flow of powders; **Flow agents** and /or **Rheological additives** to enhance film properties and minimize / eliminate surface defects by improving the flow of the molten coating; Waxes to provide slip, hardness, scratch resistance; **Matting** to reduce the gloss and/or **Texturing agents**.

The main advantages of today's powder coatings over wet coatings are:

-Durability: Powder coated surfaces are more resistant to chipping, scratching, fading, and wearing than other finishes..

- Environment Protection: Powder coatings are also highly protective of our environment. While liquid finishes contain solvents which have pollutants known as volatile organic compounds (VOCs),

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** based on Rheometric Scientific Application bulletin 19, # 902-00078* powder coatings contain no solvents and release negligible amounts, if any, of VOCs into the atmosphere

- Money Savings: Elimination of VOCs and reduction of wastes saves money.

While powder coating started as an alternative to finishing metal products only, the development of powder that can be cured at lower temperatures has allowed powder coating to expand to non-metal surfaces such as ceramics, wood and plastic applications. Technological advancements in powder coating materials application and curing methods have brought the advantages of powder coating to heat sensitive substrates, a good example is the medium density fiberboard, or MDF, a combination panel bonding particles of wood with a synthetic resin. Powder materials for MDF's can be either thermal cure products or UV-cured powders. The thermal energy melts the powder so it will flow into a level film and eventually cure, or crosslink, into a finished film. With specially formulated UV-curable powders, the melt and flow can be separated from the curing process. Minimal heat to cure the powder and exposure to ultraviolet light for just a few seconds is required for final curing and hardening of the finish.

Experimental: Since powder coatings consist of a fine powder, the sample needs to be pre-conditioned before loading into the rheometer. The best approach is to compress the powder cold into a small disc (i.e. 25mm diameter and 2mm thickness) and load the sample disc between the parallel plates of the rheometer. Important is the loading temperature. This can be room temperature for a temperature ramp test - in this case the instrument gap needs to be controlled when the sample starts to melt - or a temperature above the melting temperature, but below the curing temperature – in this case the sample can be loaded and trimmed like a polymer and the viscoelastic properties can be studied at isothermal conditions independent of the curing. This is however very often not possible, as the material starts to react as soon as the melting temperature has been reached. UV and thermoplastic powder coatings are different. For UV powder coatings the curing reaction is controlled independently from the melting process.

IMPROVING CHARACTERISTICS OF POWDER COATINGS

The key to thin coatings with high quality appearance and good substrate protection is the flow behaviour of the coating after it is applied. Optimizing both the flow and curing time at various temperatures is a challenge because these two properties work against each other. As the coating is heated, it softens physically and begins to flow. Then, a chemical reaction takes over, crosslinking occurs and the coating cures. Therefore, it is necessary to measure the time – and temperature-dependence during flow and curing simultaneously.

Also, assessment of the degree of cure (i.e. under-cure- or complete conversion of crosslinking) using rheology is possible. Studies can be made on the finished coating to determine the stiffness and toughness over a wide temperature range. The effect of ageing on coatings can also be studied to predict the long term durability as well.

Flow and coating thickness

The flow behavior and curing rates of coating formulations can be measured at a desired isothermal temperature or at a constant heating rate. Oscillatory measurements should be made at low strain amplitude to preserve the structure of the filler-resin formulation. The temperature dependence of the visco-elastic parameters (complex viscosity and loss tangent) of a typical powder coating is shown in figure 1, measured in a temperature ramp experiment followed by an isothermal phase.

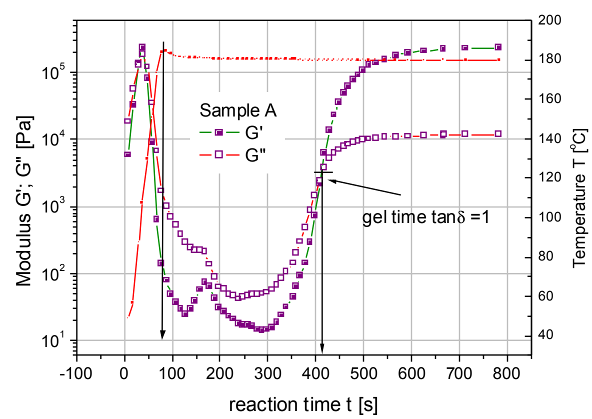

Figure 1: Cure behaviour of a typical Powder Coating. The modulus drop at 100°C is due to plastification followed by evaporating of moisture.

The flow and leveling of the coating is related to the minimum viscosity (or modulus) and the breadth of this minimum. A "poor" flowing resin has a too high minimum visosity . Moisture also greatly affects the minimum viscosity, causing the formulation to flow differently and producing voids or pinholes in the cured coating. The powder manufacturer can adjust the reactivity to allow melted powders to stay in a liquid state long enough to allow the entrapped gas to escape and then flow-over the pinholes before hardening during the final cure stages. In this case however, powders have much easier runs but sag if applied too thick. Suppliers also offer anti-outgassing formulations. In such formulations, surfactant-like compounds are added to the binder system, allowing the volatiles to escape. Either approach can prove effective in reducing outgassing-induced pinholes and craters. But the single most important factor in minimizing outgassing is reducing the amount of porosity contained in the metal structure to be coated.

Cure

Once the coating starts to cure, its viscosity increases and at the gel point approaches infinity. At this time, the flow of the coating ceases and the coating takes on the properties of a solid. A good indicator of the gel point is the point at which G'=G" or tan δ equals one.

UV-curable powders are sophisticated products. Advanced formulations melt between 40 and 70 °C while also remaining stable in a shipping container. UV-cured powders are used in industrial settings where it is practical to apply a powder, melt it in an oven, and then expose it to a radiation source. Figure 2 shows an isothermal cure of a UV cured powder coating. In order to follow the cure, fast data sampling and special transparent plates (Quartz glass or PMMA), to allow illumination of the sample with UV light need to be used (see application note AAN021 also). After a few seconds of UV-irradiation, the sample cures completely. With fast data sampling which is able to collect up to 500 data points per second, the storage and loss modulus can be monitored easily and the gel point determined.

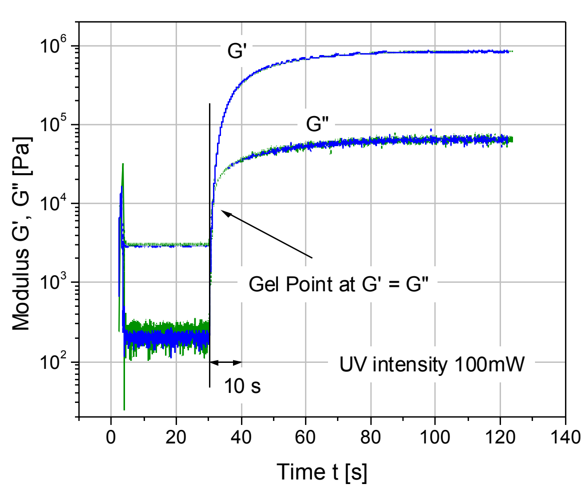

Figure 2.:UV curing with fast data sampling

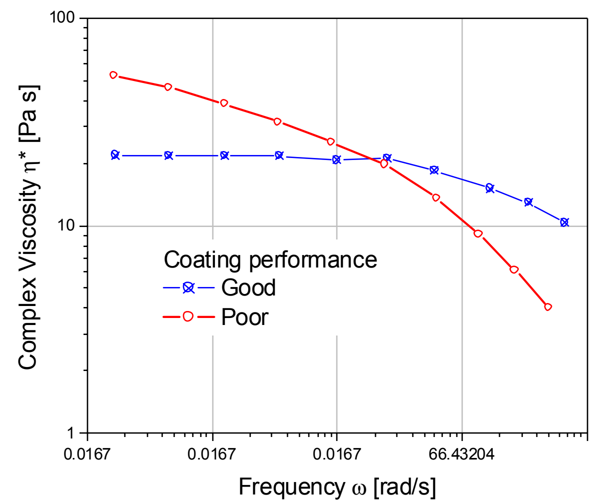

Figure 3: Flow characterization of a polyester-urethane coating

Thermoplastic powder coatings, (Figure 3) can be characterized, using dynamic mechanical analysis, in the melt under isothermal conditions to determine its flow behavior. The "poor" resin in this example did not coat the substrate uniformly. The measured complex viscosity of the "poor" sample has a higher plateau viscosity at low frequency and exhibits shear thinning (decrease of the complex viscosity with frequency) over a larger frequency range. A higher viscosity at low frequency (zero shear viscosity) stands for a higher molecular weight and the broader shear thinning range is an indication of a broad molecular weight distribution. The "good" sample with a lower MW has a lower zero shear viscosity, flows easier and provides a more uniform coat.

Dynamic Mechanical Analysis is also a very sensitive means to measure the degree of cure or crosslinking of a thermoset coating. A resin cured at 3 different temperatures is shown in figure 4. A measure of the extend of cure is the glass transition T_g. The T_g in DMA is usually evaluated at the tan δ

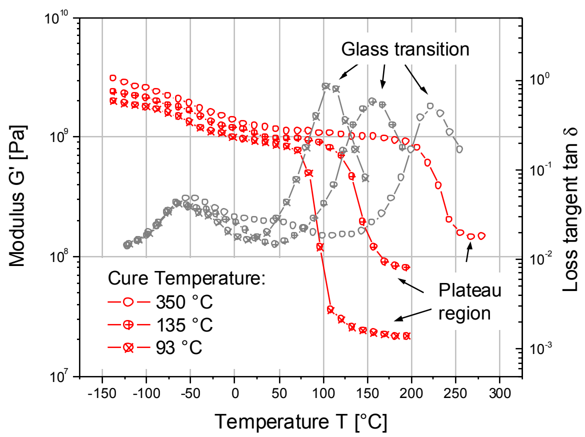

Figure 4: Effect of cure temperature on T_g and rubbery plateau of a thermoset resin

peak. With increasing cure temperature, the glass transition increases. Another measure of the degree of crosslinking is the shear modulus G' in the rubbery plateau region, above the T_g. Experimentally, this approach is difficult, as the sample will resume curing above the T_g and the crosslinking density and the storage modulus G' will increase with time.

End-use performance

Aging, fatigue and mechanical damage can greatly reduce the service life of powder coatings. Cracks, voids and debonding of the filler particles can be confirmed by dynamic mechanical analysis.

Impact modifiers are frequently added to thermoset resins to improve the impact resistance. Figure 5 shows the DMA trace (Modulus and tan δ) of a powder coating used as a automotive finish. Three major peaks in tan δ demonstrate the complexity of this coating, which has been designed for best performance such as resistance to gravel impact, scratch resistance, etc..

Impact resistance is a particular important requirement for automotive coatings. Typical impact times for gravel are in the order of 10 ms. In order to predict impact performance, the DMA traces, modulus and tan δ as a function of temperature need to be shifted to a reference time of 10 ms or a reference frequency of 10^5 s^{-1}. This means, that at a test frequency of one Hz, the impact performance has to be correlated with the low temperature behavior.

CONCLUSION

Dynamic mechanical analysis (DMA) is a very powerful tool to characterize powder coatings. Most important for powder coatings is the understanding of the flow of the material in the melt before the actual curing. Appearance, uniformity, texture, gloss etc.. depend on the flow characteristics of the powder coating during this, often very short time interval.

DMA provides also an excellent means to analyze the extend of cure and the end use performance of the final product. Impact, scratch and chipping resistance can be correlated with the modulus and loss tangent over time and temperature

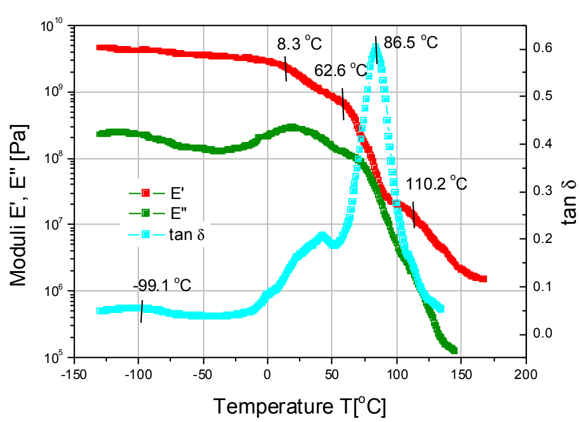

Figure 4: DMA trace of a final coat for automotive application