Lightly cured

UV powder coatings based on unsaturated allylic polyesters.
Dominique Burget, Mircea Manea, Stavros Apostolatos, Carole Mallein, Francoise Mauguiere-Guyonnet.

Allylic-terminated unsaturated polyester resins are very well suited for UV curing powder coatings, allowing systems to be formulated, which show an excellent curing behaviour under UV and visible light, cure at low temperatures, and show a very good storage stability.

Powder coatings are very attractive, environmentally friendly alternatives to liquid finishes, because they are VOC-free. UV curing resins have already been developed for applications in powder coatings. Most of these studies are concerned with acrylic materials or unsaturated polyesters (free radical curing mechanism) and epoxy materials (cationic curing mechanism).

In the presence of electron-rich double bonds, e.g. vinyl ethers, fumaric and/or maleic unsaturations also lead to a crosslinking reaction through a charge-transfer or radical mechanism [1]. Indeed, these systems (maleate or maleic-anhydride/vinyl ether) have been used in UV curable powder coatings [2,3]. Here we report on new polymers, unsaturated polyesters terminated with allylic monomers, which can be used in such systems. New, UV and visible light curable powders using these non-conventional crosslinking system based on maleic/fumaric unsaturations and allyl ethers were developed. Allyl ethers are cheaper than vinyl ethers, available in a wide variety of functionalities and structures. Thus, by using allyl ethers, the properties of the coatings can be tuned and adapted to a large variety of applications.

Composition and properties of the unsaturated resins
Amorphous unsaturated polyesters (AM 1-4) based on maleic anhydride from Interchem (Table 1) were used, which had a degree of unsaturation of about 2.15 meq db/g and a glass transition temperatures (Tg) in the range of 42-52°C (Table 1). Amorphous polyesters (supplier: Perstorp) terminated with allylic monomers are AMT-1, with trimethylpropane di-allyl ether (TMPDE), and AP-1, functionalised with pentaerythritol tri-allyl ether (APE). Their Tg’s were 30.4°C and 35.4°C, respectively. The amorphous polyester AT-1 based on TMPDE shows a higher Tg value (Tg=42.5°C), allowing its use in the powder as a crosslinker at a higher concentration. The degree of unsaturation of AT-1 is higher than that of AMT-1: 1.2 meq db/g and 0.71 meq db/g, respectively.

Several powder coatings made from mixtures of the maleic/fumaric and allyl ether polyesters were prepared (Table 1).

Photocuring mechanism of the unsaturated binders
Upon irradiation with a Xenon lamp emitting in the visible region (λ > 300 nm) and in the presence of a photoinitiator (PI) which is sensitive for these wavelengths, the characteristic infrared absorption bands at 3100 cm⁻¹ and 1645 cm⁻¹ of the TMPTE allyl double bond (dissolved in a polystyrene matrix) did not decrease (Figure 1). However, new absorption bands appeared between 3100 cm⁻¹ and 3450 cm⁻¹ as well as at 1730 cm⁻¹ and 1620 cm⁻¹. These IR absorption bands can be assigned to hydroperoxides, carbonyl, and vinyl moieties, respectively.

The sample was then exposed to passes under a UV mercury lamp. The allylic double bonds disappear slowly and the carbonyl IR absorption at 1720 cm⁻¹ increases again, at the same rate as the increase of the 1620 cm⁻¹ IR band, which is attributed to the formation of new vinyl bonds (Figure 1). This simultaneous increase can be explained by the formation of an acrylate or acrolein (Figure 2). Finally, the sample was heated at 60°C in the dark for one hour. After that, the IR absorption of the allylic bonds was decreased by 50%, whereas the carbonyl bond did not increase any further (Figure 1). Thus, working at higher temperature inhibits the formation of undesirable compounds and leads to crosslinking of the allylic double bonds.

This behaviour can be explained by the following reaction scheme involving a photooxidative crosslinking (Figure 2). The formation of undesired compounds like acrolein can be stopped if the decomposition reaction of the hydroperoxide and the quenching of the RO- radical can be speeded up by an increased temperature and by the presence of reactive double bonds. An effective crosslinking reaction through a photooxidative process can then occur without the formation of acrolein. In fact, no acrolein emission from the cured coating was detected (detection limit < 0.002 µg/m²/h).

The reactivity of the allyl ether itself is low; the role of the photoinitiator is the creation of primary radicals which can crosslink with the maleic/fumaric unsaturations. The allyl radical can also react with oxygen leading to hydroperoxides, which are involved in a second stage thermal crosslinking. The photoinduced crosslinking reaction is thus followed by a dark process accelerated by heat and catalysts.

Photocuring of the powders
The IR spectrum of the powder PM-1/AM-4 mainly shows the absorption bands of AM-4. Specific infrared absorption bands due to the allyl ether are difficult to deconvolute. Upon irradiation with UV light using a conveyor curing unit, the unsaturated bonds (of AM-4 maleic anhydride polyester and AMT-1) had disappeared after 7 passes and a new IR absorption band temporarily appeared at around 2100 cm⁻¹ (Figure 3). Furthermore, the film became insoluble in acetone and THF.

Within the same time scale, the UV-absorption spectrum revealed that the PI disappeared almost completely after 2 passes under the lamp, corresponding to approx. 50% conversion of the unsaturated polyesters. Thus, to reach the observed 100% conversion of the unsaturated polyesters, a thermal crosslinking reaction must be involved, in addition to the the photoinduced crosslinking. Increasing the amount of the allyl ether functionalities increased the reactivity of the powder (Figure 4).

Effect of a plasticizer on curing rates
Two series of experiments were made: Firstly, the powder was dissolved in THF (50% w/w) and applied with a 50 µm bar-coater. The vacuum dried sample was then irradiated. In the second case the solid powder was cast on a BaF₂ crystal (50 µm thickness) and melted in an oven at 75°C for one hour. In both cases, a clear coating was obtained, which allowed spectroscopic analysis. In both cases radiation curing was carried-out at room temperature with a UV-curing unit fitted with a 120 W/cm mercury lamp at a belt speed of...
5 m/min. The light dose was 1370 mJ/cm²/pass. For samples prepared at room temperature through solvent vaporization the conversion of the maleic unsaturation reached 90% after 15 passes under the UV lamp (Figure 5 left). The photoinitiator is bleached within 2-3 passes. On the other hand, the sample prepared by heating of the powder exhibits poor reactivity, reaching less than 40% of conversion after 15 passes (Figure 5 right). Surprisingly, the photobleaching of the photoinitiator is also slower.

The residual THF has a plasticizing effect on the powder. The diffusion of the radical species formed during the irradiation (initiating radicals from PI and propagating chain radicals) is easier in the less viscous medium. Radicals generated by PIs must react with the reactive parts in its close vicinity or recombine to yield the starting PI or in-cage photo-products. As a matter of fact, in-cage recombination products of the initiating radicals generated by PI are observed in the non-plasticized powder coating containing "Irgacure 819" as the photoinitiator.

Effect of the temperature
Samples of the powder coatings were prepared by heating the powder on a BaF₂ crystal. The curing rates were measured at temperatures ranging from room temperature (RT) up to 160°C (Figure 6). Above 100°C the curing efficiency increases sharply. At temperatures below 60-80°C the powder matrix is too hard to allow a propagative crosslinking of the polymer chains. In industrial conditions, the temperature of the powder usually is still close to 120°C when the sample arrives under the irradiation lamps. The reactivity at room temperature of the powder plasticized with THF is very close to that observed for the non-plasticized powder at 120°C. The following experiments were conducted on samples prepared by melting of the powder.

Curing rates in the presence of visible light photoinitiators
A screening of other possible photoinitiating systems for the powder coatings was carried out. It was found that the curing rate obtained with the standard "Irgacure 819+2959" can be also reached by using a multicomponent photoinitiating system like ITX/amine/maleimide (Figure 7).

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References

Results at a glance
- The curing performance of low temperature curable powder coatings based on mixtures of maleic/fumaric unsaturated polyesters with allylic unsaturated polyesters has been investigated.
- An outstanding 100% conversion of the unsaturation is obtained under irradiation with a UV or visible light.
- The versatility of the chemistry of allyl ethers allowed to obtain powder coatings having a very good physical storage stability and showing very good flowing properties.
Figure 1: Changes in the IR spectrum of a sample of TMPTE/TPO in a polystyrene matrix upon irradiation. (5 min. with a visible Xenon lamp, 10 passes under a 120W/cm mercury lamp, and subsequent heat treatment at 60°C in the dark for 1 hour.)
Figure 2: Reaction scheme for the crosslinking of allyl ethers
Figure 3: Changes in the IR absorption spectrum upon irradiation of the powder PM-1/AM-4 prepared by solvent evaporation. Thickness ~50µm. Light source: UV mercury lamp, Io = 1410 mJ/cm2/pass
Figure 4: Curing rates at 120°C of the powder samples prepared by melting before exposure to light. The light source is a mercury UV lamp (230 mW/cm²). Film thickness 25 µm
Figure 5: Double bond conversion of the powder AM4-AMT1 versus the number of passes under the 120 W/cm mercury lamp. The sample was prepared by solvent evaporation (left) or melting (right). In both cases, the time dependent concentration of the remaining photoinitiator ("Irgacure 819") is monitored by UV-visible spectroscopy in real-time.
Figure 6: Disappearance of the double bonds upon irradiation with UV light in PD1-AM4 + 2.4% I819 /0.6% I2959 at various temperatures. Rate of polymerization (Rp) and degree of conversion after 20s of irradiation. Io= 282mW/cm2. Film thickness 55 µm
Figure 7: Curing rates of the powder PM-3/AM-4 in the presence of several photoinitiating systems. Light source is the mercury lamp of the UV-curing unit working at 5 m/min
Table 1: Composition and properties of the unsaturated polyesters based on maleic anhydride and typical composition of some of the powders

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<th>Code No</th>
<th>Acid number (mg KOH/g)</th>
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</tr>
<tr>
<td>PM1/AM-4</td>
<td>AM-4/AMT-1 (70/30)</td>
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<tr>
<td></td>
<td>I819 + I2959 (2.4%/0.6%)</td>
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<tr>
<td>PM1/AM-4</td>
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<td>I819 + I2959 (2.4%/0.6%) additive (1.5%)</td>
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<tr>
<td>PM1/AM-4</td>
<td>AM-4/AT-1 (50/50)</td>
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<td>I819 + I2959 (2.4%/0.6%) additive (1.5%)</td>
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