

Photocationic-curable powder coatings

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Summaries

Photocationic-curable powder coatings

The UV-curable powder coatings allow the finishing of temperature-sensitive substrates such as wood, MDF (medium-density fibreboard), plastics and paper. The binder system is mostly comprised of unsaturated polyester, a vinyl ether and acrylic polyurethane. The curing mechanism consists of free radical polymerisation of the double bonds.

In comparison with free radical UV curing, the cationic-initiated UV-curing technology offers the advantages of insensitivity to oxygen and lower film shrinkage. Epoxides are one of the most important and widely used classes of resins in the field of cationic UV-curable powder coatings. Epoxy systems do not require any additional curing agent, they cure within seconds and have unlimited working times.

For photocationic curable powder coatings, solid epoxy resins have been used. However, such a system has some disadvantages: the epoxy value is too low to obtain sufficient cross-link density. This problem may be overcome by the use of a binder having more epoxide rings in the oligomer structure (eg epoxypolyesters). In the present study, a series of solid epoxypolyesters were prepared by polycondensation of glycols, tetrahydrophthalic anhydride and dicyclopentadiene, followed by the epoxidation of the double bonds in unsaturated polyester. The epoxypolyesters were subject to photoinitiated cationic polymerisation. The evaluation of the film performance was also carried out. The coatings prepared from these epoxypolyesters exhibited good hardness, impact strength and adhesion.

Les revêtements en poudre à séchage photocationique

Les revêtements UV en poudre facilitent la finition des substrats qui sont sensibles aux températures élevées, tels que les substrats de bois, de MDF (de fibres de densité moyenne) de plastiques et de papier. Le système de liants est composé pour la plus grande partie de polyesters non saturés, un éther vinylique et un polyuréthane. Le mécanisme de séchage consiste en la polymérisation de doubles liaisons par radicaux libres.

Par rapport au séchage UV à radicaux libres, la technologie du séchage UV à initiation cationique offre les avantages de l'insensibilité à l'oxygène et d'un moindre rétrécissement du film. Les époxydes sont parmi les types de résine les plus importants et les plus utilisés dans le domaine des revêtements en poudre UV cationiques. Les systèmes époxy ne requièrent pas d'agent de séchage additionnel, ils séchent en quelques secondes et offrent un temps de travail illimité. On a utilisé des résines époxy à l'état solide comme revêtements en poudre à séchage photo cationique. Cependant ce système a des inconvénients : la valeur de l'époxy est trop basse pour donner une densité suffisante de réticulation. Ce problème peut être éliminé par l'usage d'un liant qui ait plus d'anneaux époxydes dans la structure oligomère (comme, par exemple les epoxy-polyesters). Au cours de cette étude on a préparé une série d'époxy-polyesters par la polycondensation des glycols, tétrahydrophthalique anhydride et dicyclopentadiène, suivi de l'époxydation des doubles liaisons dans le polyester non saturé. Les epoxy-polyesters ont subis une polymérisation à initiation cationique. On a aussi fait une évaluation de la performance du film. Les revêtements préparés à partir de ces epoxy-polyesters ont fait preuve d'une bonne dureté, un bon résistance au choc et une bonne adhérence.

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Introduction

Photopolymerisations initiated by ultra-violet (UV) light have received considerable attention for the rapid, solvent-free curing of polymer films. These solvent-less polymerisations proceed rapidly at room temperature with a fraction of the energy requirements of thermally-cured systems. The recent surge in applications of UV-initiated photopolymerisations has been motivated by at least two factors: environmental concerns about the production of volatile organic compounds (VOCs) emissions, and the need for high-speed reactions to enhance production rates. As a result, UV-initiated photopolymerisations are finding application in a variety of areas, including coatings, inks, adhesives, and electronics.¹⁻⁴ Moreover, this gentle curing method allows even heat-sensitive substrates to be coated. To date, however, these advantages have been confronted with a number of disadvantages. Relatively high materials and plant costs, complicated formulation, poor wetting and shrinkage reduce the adhesion to metals, and problems with pigmentation as well as a limitation to flat substrates have been the principal arguments against further development.^{5,6} However, the technical innovations and more attractive pricing have, in recent years, opened up new fields of application, especially in UV-curable powder coatings.⁷

Although the UV-curable powder coatings are not yet widely used as thermosetting powders, the work performed so far has already shown that the combination of environmentally-friendly powder coating technology and UV curing can give a coating system which offers the following advantages over thermosetting powders:

- high-cure speed diminishes curing space requirements and energy consumption;
- room temperature cure enables the coating of heat-sensitive substrates such as wood, medium-density fibreboard (MDF), thermoplastics, and paper;
- because the film formation and curing are independent processes, UV powder technology provides orange peel-free films with reduced cure time. For instance, flow and levelling can be achieved by infrared (IR) irradiation followed by UV irradiation to achieve polymer cross-linking by a free radical or a cationic mechanism (see Figure 1).

Frost & Sullivan, the international marketing and consulting company, recently

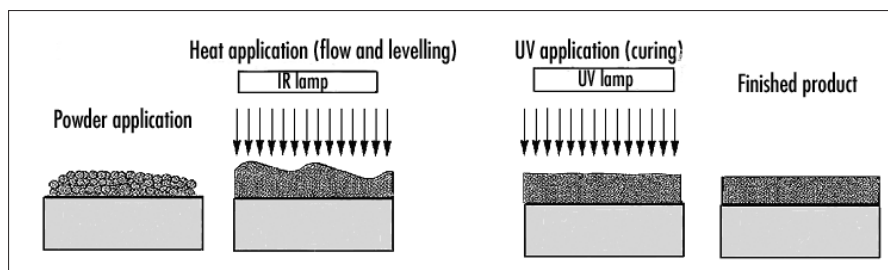


Figure 1: Generalised scheme for UV-curable powder coating

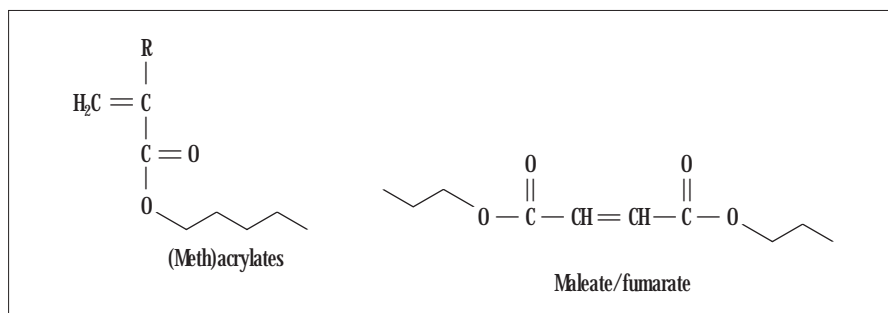


Figure 2: The main types of binders for UV-curable powder coatings

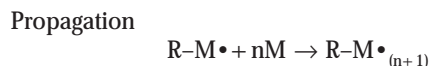
reported that “the powder market is being revolutionised by UV-curable powder coatings”. It is certain that UV-curable powder technology opens new markets and probably in the near future the use of UV powders will expand considerably.^{8,9}

State-of-the-art

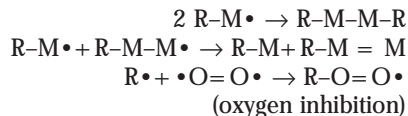
Chemistry of UV-curing coatings

Photochemical cross-linking of UV-curable powder coating occurs by a free-radical mechanism with unsaturated moieties or by a cationic mechanism with epoxy or vinyl ether functionalities.^{9,10}

Free radical mechanism



Chain termination



To-date, most of the work on UV-curable powder coatings has focused on free radical systems based primarily upon solid polyester (meth)acrylate and solid maleate/fumarate unsaturated polyesters (see Figure 2).

These monomers polymerise rapidly and are easily modified at the ester functionality, allowing materials with a variety of properties to be obtained. However, acrylates are not without their problems

and shortcomings. Acrylates are relatively volatile, have an unpleasant odour, present potential health hazards, and have to be modified when used for powder coatings formulations.^{1-3,5} Solid oligomeric acrylates are much less volatile, but exhibit a tendency to agglomerate during storage as a powder. Finally, free radical photocuring is inhibited by oxygen and often must be carried out under an inert atmosphere such as nitrogen or in the presence of additives, which inhibit oxygen absorption.^{1,2,6}

Cationic mechanism

Cationically-cured resin systems are initiated and propagated by a chemical mechanism which is outlined in Figure 3. Photolysis of diaryliodonium salt (used as an example) leads to a super acid which initiates a cationic polymerisation of epoxies or vinyl ethers^{4,11} (see Figures 4 and 5).

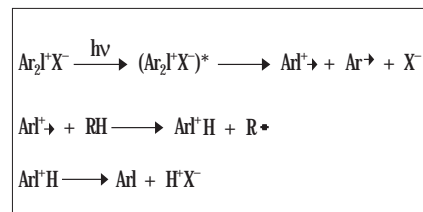


Figure 3: Mechanism of photolysis of diaryliodonium salts

UV-initiated cationic cross-linking exhibits several advantages compared with the free-radical cross-linking previously discussed. First, the cationic cross-linking is not inhibited by oxygen.^{2,5,6} Therefore, it is not necessary to blanket the system with nitrogen to obtain rapid

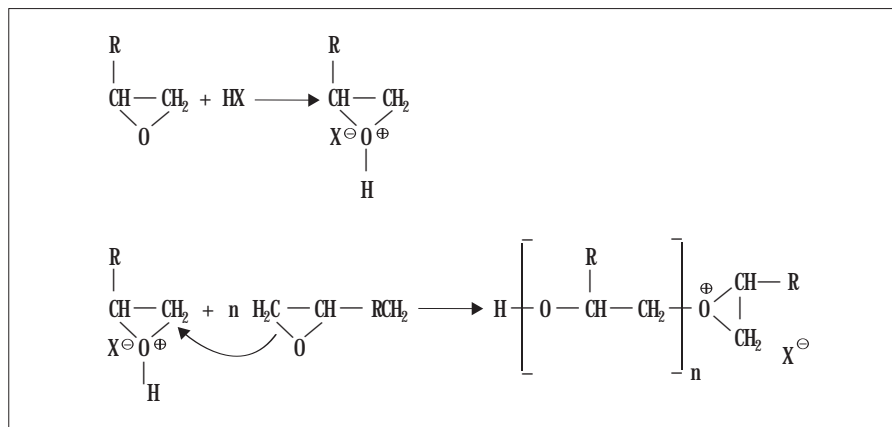


Figure 4: Mechanism of cationic polymerisation of epoxies

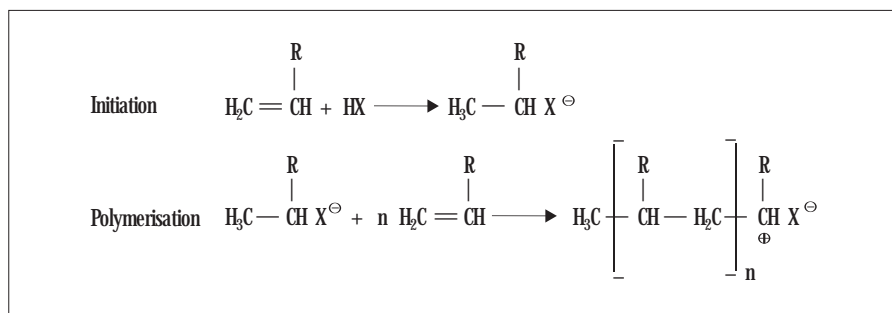


Figure 5: Mechanism of polymerisation of vinyl ethers

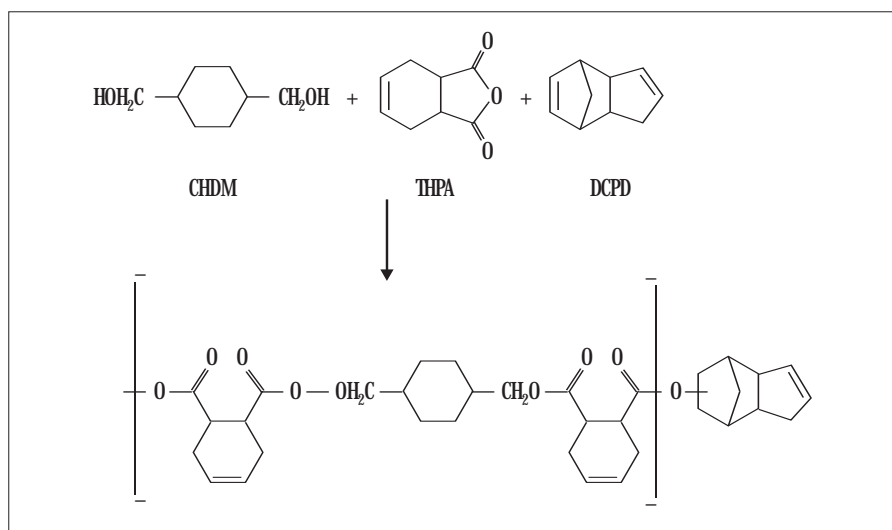


Figure 6: Raw materials used for the synthesis of epoxyesters

cure rates. Second, in contrast to the free radical polymerisation which experiences a rapid decrease in rate when the light source is removed (due to radical-radical termination reactions), the propagation of UV-curable coatings occurs after UV exposure. The cationic reactions proceed long after the irradiation has ceased, and penetrate recessed areas that the light can not reach. This phenomenon is called 'dark cure'. Dark cure is due to the long-lived initiating species or cationic species. It was found that the dark cure process represents a significant part of the overall process. Dark cure can improve the coating

properties such as adhesion and hardness. Finally, the cationic technique may be used to polymerise important classes of solid monomers and oligomers, including epoxides and vinyl ethers. These monomers exhibit very low vapour pressures, relatively low melt viscosities, negligible toxicity, and polymerise to form films that exhibit excellent clarity, adhesion, abrasion resistance and chemical resistance.²

Discussion

Concluding from the available data in the literature and from conventional

powder coatings, it is recognised that in order to get hard and flexible surfaces and low application viscosities, the glass-transition temperature (T_g) of binders should be about 50 to 60°C, with a melting range of 77 to 80°C.¹² Therefore, the resins to be used as binders are usually narrow in molecular-weight distribution, with a functionality range from 350g to 1000g of resin. The most commonly employed solid multi-functional binder for UV-induced cationic curing powder coatings are solid epoxy resins based on bisphenol A. However, they have some disadvantages: aromatic epoxides are not reactive enough and have a tendency to yellowing. Moreover, they give poor cross-link density after curing. Cycloaliphatic epoxides provide a number of important advantages in coating applications, including a fast cure response, excellent adhesion to a wide variety of substrates, flexibility, excellent gloss, low potential for skin irritation, low shrinkage, good weatherability, and good electrical properties. However, most of the commercially-available cycloaliphatic epoxides are liquid and therefore cannot be used as binders for powder coatings.¹³ This problem may be overcome with the use of a binder having epoxide rings in the oligomer structure (eg epoxypolyesters).

In the present study, a series of solid unsaturated polyesters were prepared by polycondensation by varying the amounts of 1,4-cyclohexyldimethanol (CHDM), neopentyl glycol (NPG), hexahydrobisphenol A (HHBA) and 1,4-tetrahydrophthalic anhydride (THPA) (see Figure 6).

Unsaturated polyesters were optionally modified with dicyclopentadiene (DCPD) (see Figure 7).

Properties of the resultant solid unsaturated polyesters are listed in Table 1. It can be seen from this Table that the polyester of example 4 was provided as a comparative example with a melting point that was too low. Examples 3 and 5 had melting points that were too high. Examples 1, 2 and 6 had melting points of above 90°C and appeared suitable (after epoxidation) for further processing in powder coating applications.

Solid unsaturated polyesters 1, 2 and 6 were epoxidised with peracetic acid (see Figure 8).

However, all epoxidised polyesters modified with DCPD have a tendency to gelation at relatively low temperatures and formed an emulsion during work-up. This is probably associated with the instability of the epoxide in the terminal DCPD ring. This behaviour excluded the

Experimental

Processing procedure for solid unsaturated resin

Solid unsaturated polyester modified with DCPD (1, 2): inert gas sparge, a thermometer, and the appropriate partial condenser CHDM (or NPG) and half of the first stage THPA were added to a reactor equipped with an agitator. The mixture was heated up to 130°C to achieve a slurry of the ingredients, and then the remaining half of the THPA, DCPD and esterification catalyst were added. The heating was continued to a maximum reaction temperature of 200°C and held to obtain an acid number of five or less and the desired viscosity. Then the polymer was cooled down to 180°C and discharged from the reactor.

Solid unsaturated polyester (3 to 6) based on CHDM, HHBA and THPA was prepared in a manner similar to that of the unsaturated polyester modified with DCPD. The properties of the obtained polyesters are shown in Table 1.

Processing procedure of epoxidation.

Solid unsaturated polyester was dissolved in toluene or methylene chloride and was epoxidised with 40% peracetic acid at 40°C for six hours. After completion of the reaction, acetic acid was removed by washing with 10% NaHCO₃ and with water. The solvent was distilled off from the resin. Yields were 10 to 15% for 1 and 2, 88 to 90% for 6. The properties of the obtained epoxy polyesters are shown in Table 2.

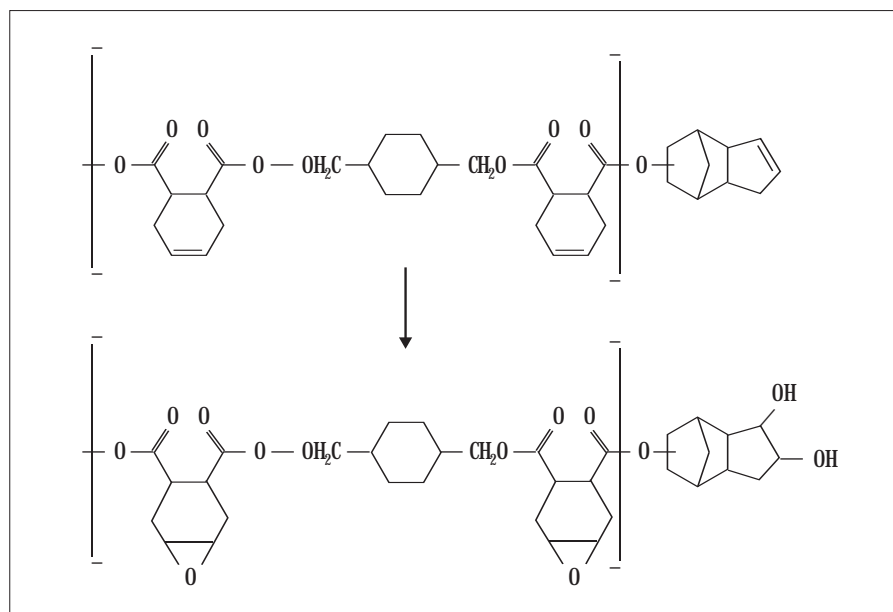


Figure 7: First stage – synthesis of solid unsaturated polyester

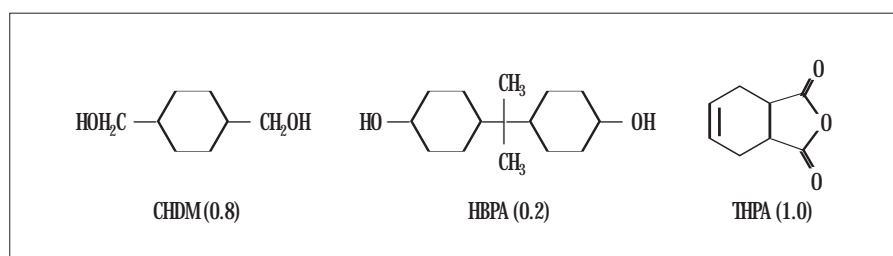


Figure 8: Second stage – epoxidation of double bonds

use of this type of resin as a binder for powder coatings. The use of the epoxy polyester based on CHDM, hexahydro-bisphenol A (HHBA) and THPA, overcame this problem.

The obtained unsaturated solid polyester synthesised from CHDM, HHBA and THPA was then epoxidised with per-

acetic acid in good yield (88 to 90%). The epoxy polyester was subjected to photoinitiated cationic polymerisation. An evaluation of the film performance was also carried out. The coatings prepared from that epoxy polyester exhibited good hardness, impact strength and adhesion.

Table 1: Unsaturated polyester properties

Ex	Raw materials (mole) ¹					Acid no	MP (°C)	ICI viscosity (poise/°C)	T _g (°C)	Mn ²
	THPA	DCPD	HHBA	CHDM	NPG					
1	1.125	0.161	–	1.125	–	10.3	109	23/140	57	4130
2	1.125	0.161	–	–	1.125	4.9	98	20/140	55	4259
3	0.52	–	0.09	0.465	–	28	116	66/125	67	4925
4	0.50	–	0.12	0.6	–	4.0	87	45/130	50–65	4020
5	0.50	–	0.4	0.3	–	3.5	133	–	–	4300
6	0.76	–	0.14	0.66	–	4.4	105	–	65	4321

¹ Esterification catalyst (Fascat 4100, Atochem), 0.2% of total weight

² Mn is theoretical number average molecular weight

Table 2: Epoxy polyester properties

Epoxidation example	MP (°C)	ICI viscosity (poise/°C)	T _g (°C)	Acid Number mgKOH/g	Epoxy value eq/100g	Yield % ¹	Remarks
1	80	10.3/140	55	8.2	0.16	10	Emulsion during work-up
2	85	22/140	–	7.9	0.15	12	Emulsion during work-up
6	100	35/140	49	5.1	0.19	88–90	

¹ Separated yield

Preparation of powder coating formulation

Cationically-cured formulations were prepared in a similar fashion to their free radically-cured counterparts, with a couple of exceptions. Basic and acidic contamination should be avoided. Surface cure was evaluated by lightly rubbing a cotton ball over the coating surface immediately after the panel exited the UV curing unit. The coating was considered surface-cured if no cotton fibres remained attached to the coating surface. The most important variable to control was the interval of time between UV cure and evaluation. As photoinitiator, commercially-available triphenyl sulphonium hexafluorophosphate (TSH) was used (see Figure 9).

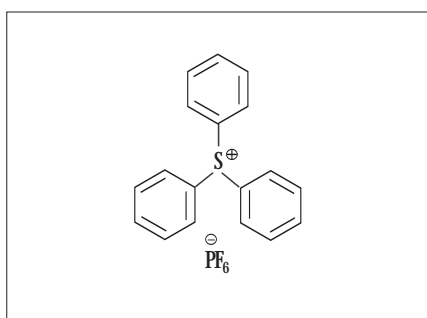


Figure 9: Triphenyl sulphonium hexafluorophosphate (TSH)

The components (see Table 3) were extrusion-blended at 100°C. The extrudate was ground to less than 90 microns and applied on to metal or MDF. The substrates were heated in an oven at 100°C or by infrared (medium wave) lamp for five minutes. The substrates were then allowed to cool to room temperature and then cured by UV light at 2J/cm² for 50 seconds. Film formation and the degree of cure were assessed visually and by MEK rubs, respectively (see Table 4). The results show that the application of this system on MDF, thermoplastics and on hardwood is acceptable.

Table 3: Cationic UV-curable clear powder coating formulation

Component	Weight parts
Epoxy polyester 6	9.0
Photoinitiator ¹	1.0
Flow agent ²	1.5
Viscosity suppressant ³	5.0

- 1 TSH
2 BYK 361 (Byk Chemie)
3 Oxymelt A-4 (Estron Chemical)

Conclusions

For photocationic-curable powder coatings, solid epoxy resins have been used.

Table 4: Properties of the cationic UV-curable clear powder coatings

Flow (visually determined)	Good
Appearance (visually determined)	Good
Acetone resistance ¹	++
MEK resistance ¹	++
Ability to be sanded	Good
Adhesion	Good
Pencil hardness	2H-4H
Flexibility (Conical Mandrel)	Pass 2mm
Impact (Du Pont tester 1kg/cm)	Pass 50

1 ++ no damage after 100 double runs

However, such systems have some disadvantages. The epoxy value is too small to obtain a good cross-link density. This problem may be overcome by the use of a binder having more epoxide rings in the oligomer structure (eg epoxy polyesters). In the present study, a series of solid epoxy polyesters were prepared by polycondensation of glycols, tetrahydrophthalic anhydride and dicyclopentadiene, followed by the epoxidation of double bonds in unsaturated polyester. The epoxy polyesters were subjected to photoinitiated cationic polymerisation. All epoxidised polyesters modified with DCPD have a tendency to gelation at relatively low temperatures and an emulsion is formed during work-up. This is probably associated with the instability of the epoxide in the terminal DCPD ring. This behaviour excluded the use of this type of resin. The use of the epoxy polyester based on CHDM, HHBA and THPA can overcome this problem. The resin has good application properties. The coatings prepared from this epoxy polyester exhibited good hardness, impact strength and adhesion.

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References

1. Kloosterboer J G, *Adv Polym Sci*, **84**, 1, 1988
2. Roffey C G, *Photopolymerization of Surface Coatings*, Wiley, New York, ISBN 0 4711 1063 8, 1981
3. Pappas S P, *Radiation Curing: Science and Technology*, 109-15,

Plenum Press, New York, ISBN 0 3064 3999 9, 1992

4. Crivello J V, *Adv Polym Sci*, **62**, 1, 1984
5. Lapin S P, 'Radiation curing of polymeric materials', (ed) C E Hoyle and J F Kinstle, ACS Symposium Series, **363**, 417, American Chemical Society, Washington DC, ISBN 0 8412 1730 0, 1989
6. Reiser A, *Photoreactive Polymers*, 95-115, Wiley, New York, ISBN 0 4718 5550 2, 1989
7. Griese Ch and B Carlson, 'Development in UV-curable powder coatings', Technical Conference Proceedings, Radtech 2000, 658-68, 9th to 12th April 2000
8. Wicks Z W, E N Jones and S P Pappas, *Organic Coatings, Science and Technology*, **1**, 140-50, Chapter III, Wiley, New York, ISBN 0 4716 1406 8, 1992
9. Decker C, 'UV curing chemistry: Past, present and future', *J Coat Tech*, **59**, 97, 1997; Thames S F, J W Rawlins, 'A review of ultraviolet-curable powder coatings', *Powder Coating*, **10**, 19, 1996
10. Lohse F and H Zweifel, 'Photocrosslinking of Epoxy Resins', *Adv Polym Sci*, **78**, 268, 1986
11. Crivello J V and K Dietliker 'Photoinitiators for cationic polymerization', *Chemistry and Technology of UV & EB Formulation for Coating, Inks and Paints*, **3**, Chapter II, 327-478, SITA Technology Ltd, London, ISBN 0 4719 8235 0, 1999
12. Wicks Z W, E N Jones and S P Pappas, *Organic Coatings, Science and Technology*, **2**, 115-25, Wiley, New York, ISBN 0 4715 9893 3, 1994
13. Wu S, M T Sears and M D Soucek, 'Synthesis of reactive diluent cationic cycloaliphatic epoxide UV coatings', *Polymer*, **40**, 5675, 1999