

UV-curable powder coatings containing interpenetrating polymer networks (IPNs)

Saeid Bastani^{a,b}, Siamak Moradian^{b,*}

^a *Iran Color Research Center (ICRC), Surface Coatings and Corrosion Department, No. 32, Shahid Afshari St., Hemmat Highway Jun, Banihashem Sq., Tehran, Iran*

^b *Polymer and Color Engineering Department, Amirkabir University of Technology, No. 424, Hafez Ave., Tehran, Iran*

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Abstract

In spite of obvious advantages of radiation curable powder coatings some of their physical and mechanical properties such as impact resistance, flexibility, hardness and tensile strength are poorer than thermally curable powder coatings. It is believed that UV-curable powder coatings containing interpenetrating polymer networks (IPNs) inherently have the ability to develop these properties. In the present study, two different UV curing systems (i.e. free radical and cationic types) were used in order to obtain the prospective IPNs. Interesting properties are to be found by these coatings founded in the different possible morphologies caused by phase separations. These modified radiation curable powder coatings showed significant improvements in the mechanical and physical properties of such powder coatings.

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1. Introduction

Since the introduction of powder coatings, some 30 years ago, there has been continuous attempts to lower the temperature of curing [1,2]. Reduction of the cure temperature of Polyester–Triglycidyl Isocyanurate (TGIC) systems from 200–220 °C to 160 °C with acceptable levelling properties has proved to be reachable [2]. However, for certain applications in the automotive, wood and plastic industries, even a cure temperature of 160 °C is too high. In most cases, the cure temperature for these applications should be below 100 °C.

One approach to solve such a problem is the use of radiation curing systems instead of thermally activated reactions. Recently, several publications concerning UV powder coatings have appeared [3–5,8]. The use of UV-curable powder coatings may have the following advantages:

- essentially no emission of VOC;
- fast curing speeds;

- minimal health risk;
- independency of the flow system from the cure system.

UV-curable powder coatings were thought to provide excellent capabilities in coatings for wood. However, the first reported commercial application was on metal substrates [9].

UV-curable powder coatings can be cured via both the cationic and the radical mechanisms. In radical cure systems various resins such as unsaturated polyester, polyurethane acrylate and maleate vinylether have been used [4,5]. In the cationically cured systems however, epoxy type resins including, bisphenols, novalac modified bisphenols, cycloaliphatic epoxides, glycidylmethacrylates and glycidyl acrylics have dominantly been used [6].

Despite the advantages of these systems, some of their physical and mechanical properties such as impact resistance, tensile strength, flexibility and hardness are poorer than their thermally cured equivalents. Some of these properties have been recently improved by varying the type and amount of crosslinkers [8].

In the present study use were made of interpenetrating polymer networks (IPNs), in order to improve such physi-

* Corresponding author. Tel.: +98 21 6468243; fax: +98 21 6468243.
E-mail address: moradian@cic.aut.ac.ir (S. Moradian).

cal and mechanical properties. An IPN is most commonly described as a blend of two or more polymeric networks in which at least one of the networks has been synthesized and/or crosslinked in the intimate presence of the other [9]. One of the methods of synthesizing IPNs, is by the “simultaneous” or “SIN” technique. In SINs, monomers, oligomers, crosslinkers and initiators are mixed together and the polymerization and crosslinking is forced to occur simultaneously.

These networks were used in coatings by Frisch et al. [11] 20 years ago. IPNs can be prepared by bulk, solution, or emulsion polymerization. Some permanent entanglements between the different crosslinked networks are inevitable in any intimate mixture of crosslinked networks.

These permanent entanglements would restrict segmental motion, simulating covalently bound chemical crosslinks.

The IPNs synthesized to date exhibit varying changes of phase separation depending primarily upon the compatibility or miscibility of the components present in the polymer mix. Phases, which vary in size, shape, sharpness, and degree of continuity, have a profound effect on physical and mechanical properties such as the modulus and the glass transition temperature [12–14].

2. Experimental

2.1. Materials

All used materials are given in Table 1.

2.2. Preparation of free radical UV-curable powder coatings (FRUVPC)

The clear formulation containing 81.6 wt% Uracross P3125, 16.7 wt% Uracross P3307, 1 wt% Iragacure 184, and 0.66% BYK 361 were mixed by melt extrusion [8].

2.3. Preparation of cationic UV-curable powder coatings (CUVPC)

Equal parts of “VEctomer” and “GT6259” were mixed together and then 3 wt% of UVI 6974, together with the

Table 2
Composition of IPN UV-curable powder coatings

Sample no.	Free radical UV-curable powder coatings (parts by weight)	Cationic UV-curable powder coatings (parts by weight)
FRUVPC	100	0
IPN-1	90	10
IPN-2	80	20
IPN-3	70	30
IPN-4	60	40
IPN-5	50	50
IPN-6	40	60
IPN-7	30	70
IPN-8	20	80
IPN-9	10	90
CUVPC	0	100

photosensitizer and the palsticizer were added. Finally these composites were mixed by melt extrusion [6].

2.4. Preparation of IPN UV-curable powder coatings

Both free radical UV-curable powder coatings and cationic UV-curable powder coatings were blended at various weight ratios to prepare the IPN powder coatings (Table 2).

No pigment was added to these formulations. All coating formulations were made according to a standard procedure. Extrusion of the premix took place at 80 °C, 200 rpm in a twin-screw extruder. The powder coatings were sprayed electrostatically with a corona gun on to the substrate. The flowing and curing conditions were as follows:

Flow: IR-radiations (32 kw/m²) (100 sec).

Cure: UV exposure (7 m/min at 2 × 80 w/cm medium pressure Hg lamp). The coatings were then postcured in a 100 °C oven for 5 h.

2.5. Testing of IPN powder coatings

The Gardner impact resistance (performed according to ASTM D 2794-69), pendulum hardness, adhesion, and MEK resistance were performed on coatings applied to a film thickness of 75–100 µm over Q-panels. The salt spray resistance was determined according to ASTM B117. The Tgs were determined on a Perkin-Elmer DSC equipment over the range of –100 to 200 °C at a heating rate of 10 °C/min.

3. Results and discussion

Free radical and cationic UV-curable powder coatings have very different crosslinking mechanisms. In free radical, polymerization the double bond is opened by the free radicals generated by photoinitiator, whereas in cationic UV curing, the epoxy rings are opened by the cations generated by the UV radiation activated photoinitiators.

Table 1
Materials

Designation (component composition)	Suppliers
Uracross P3125	DSM
Uracross P3307	DSM
Cyracure UVI 6974 (onium salt photoinitiator)	Union Carbide
BYK 361	BYK Chemie
VEctomer (aromatic urethane divinyl ether)	Allied Signal Co.
GT 6259 (bisphenol A/epoxy cresol novolac)	Ciba-Geigy
Photosensitizer (cumene hydroperoxied)	–
Plastisizer (epoxidized soya oil)	–
Iragacure 184	Ciba-Geigy
BYK 365	BYK Chemie
Araldite GT 7004 (epoxy resin)	Ciba-Geigy
Uralac 5125 (polyester)	Ciba-Geigy

Table 3
Physical and mechanical properties of IPN powder coatings

Designation	Direct impact (in. lbs)	Konig hardness (sec)	Cross hatch adhesion	Flow (°C)
FRUVPC	5	210	1B	110
IPN-1	20	210	2B	110
IPN-2	35	203	3B	110
IPN-3	78	201	4B	110
IPN-4	112	194	5B	110
IPN-5	140	183	5B	110
IPN-6	150	177	5B	110
IPN-7	160	169	5B	110
IPN-8	160	133	5B	110
IPN-9	160	104	5B	110
CUVPC	160	90	5B	110
Hybrid PE-Epoxy ^a	60	210	5B	180

^a The formulation contains a 50:50 ratio of resin:crosslinker 50:50 Uralac 5125 and epoxy resin (Araldite GT 7004), flow additive BYK 365 and benzoin. Cured 12 min at 180 °C.

3.1. Properties of IPN UV-curable powder coatings

Table 3 shows some properties of the differently prepared IPN powder coatings. It is evident from this table that it is possible to formulate IPNs with the optimal required properties. The tough cationic UV-curable powder coatings (i.e. epoxy-urethane divinyl ether) exhibited better flexibility together with a corresponding softness than the brittle, hard free radical UV-curable powder coatings. The IPN compositions high in CUVPC content were therefore softer and more flexible than those high in FRUVPC content (Table 3).

The adhesive strength is believed to be related to the hydrogen bonding capabilities of the corresponding network compositions (Table 3). Therefore, the IPN compositions high in CUVPC content exhibited better cohesive and finally adhesive strength than the others.

The salt spray resistances of the IPN UV-curable powder coatings were also measured, the results of which are given in Table 4. The FRUVPC have higher crosslink densities than CUVPC, hence the IPN coatings formulated with higher FRUVPC content exhibited excellent salt spray resistances (Table 4).

Table 4
Properties of IPN powder coatings

Designation	MEK resistance ^a	Salt spray (mm) (240 h)
FRUVPC	100	2
IPN-1	100	2
IPN-2	100	2
IPN-3	100	2
IPN-4	100	2
IPN-5	100	2
IPN-6	87	2
IPN-7	74	4
IPN-8	40	5
IPN-9	32	10
CUVPC	20	15
Hybrid PE-epoxy	±	12

^a ± surface slightly damaged.

The MEK resistances of the IPN UV-curable powder coatings were measured in double rubs (Table 4). The CUVPC require post curing for better MEK resistance. Therefore, IPN coatings, which were formulated with high FRUVPC contents exhibited better MEK resistances.

3.2. Morphology of IPN UV-curable powder coatings

All of the IPN UV-curable powder coatings exhibited only one Tg (Table 5). The existence of only one single Tg indicates the formation of an IPN and rules out phase separation possibilities.

The compatibility of polymers have been determined by the compatibility factor (θ) by many workers [12,14]. This factor was theoretically derived from the *DiBenedetto* equation by Frisch et al. [12]. The form of the modified equation is as follows:

$$\frac{T_g - T_g(\text{av})}{T_g(\text{av})} = \frac{-\theta}{1 + \theta} \quad (1)$$

Table 5
Effect of composition of the IPN powder coatings on Tg

Designation	Tg (K)	Tg (av) (K) ^a	Copolymer ^b Tg (K)	θ^c
FRUVPC	320	—	—	—
IPN-1	318	320.8	320.7	0.009
IPN-2	319	321.6	321.4	0.008
IPN-3	321	322.4	322.1	0.004
IPN-4	324	323.2	322.9	−0.002
IPN-5	331	324.0	324.7	−0.021
IPN-6	336	324.8	324.5	−0.033
IPN-7	332	325.6	325.3	−0.019
IPN-8	326	326.4	326.2	0.001
IPN-9	327	327.2	327.0	0.0006
CUVPC	328	—	—	—

^a Eq. (2).

^b $1/T_g = w_1/T_{g1} + (1 - w_1)/T_{g2}$ (Fox equation).

^c Eq. (1).

Many workers [13] have suggested that the measured T_g of the resulting IPN is lower than the calculated T_g (av) of the two separate polymers obtained from Eq. (2).

$$T_g(\text{av}) = w_1 T_{g1} + (1 - w_1) T_{g2} \quad (2)$$

This would mean that as the values of calculated θ approach zero the compatibility would approach completion.

4. Conclusions

The present study showed that some of the properties of IPN UV-curable powder coatings such as adhesion, hardness, impact strength, solvent (MEK) resistance and the resistance to salt spray were better than the separate individual UV-curable powder coating compositions. It seems that through careful selection of the type and the amount of free radical and cationic components to form IPN UV-curable powder coatings it is possible to engineer the required properties.

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Further reading