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SHORT REPORTS

Sensitization Capacity of Polyester Methacrylate in Ultraviolet Curing Inks Tested in the Guinea Pig

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Abstract. One of the prepolymers used in Ultraviolet (UV) curing ink formulations is acrylated polyester. The prepolymer investigated is a dimethacrylated polyester, thus a saturated polyester terminated with methacrylic groups. In conventional UV-curing coatings the prepolymer commonly used is an unsaturated polyester. Three of six workers with dermatitis from UV-curing inks in printing plants had positive test results from the polyester methacrylate present in the inks used. The sensitizing capacity, performed with the "Guinea pig maximization test", shows polyester methacrylate to be a moderate sensitizer.

Key words: Acrylated prepolymers; Methylacrylate; Methyl methacrylate; Polyester methacrylate; Sensitization capacity; Ultraviolet curing ink; Unsaturated polyester

Ultraviolet light-cured inks have been formulated and used successfully in letterpress, lithographic, gravure and flexographic printing as a substitute for the solvent-based printing inks currently used. These new ultraviolet light (UV)-cured inks offer advantages other than the elimination of solvent emission, notably: a combination of excellent film properties with fast printing speeds; curing at ambient temperature with less damage to heat-sensitive substrates such as plastics, textiles, wood and paper; and a reduced energy consumption. The great interest in their development is shown by the large number of patient citations describing various compositions that can be cured by ultraviolet light (9, 11).

The unsaturated polymers used in the formulation of UV-curable resins can be divided into two broad classes: unsaturated polyester resins and polymers containing pendent unsaturation.

In unsaturated polyester resins, the monomer or "solvent", primarily styrene or vinyl toluene, copolymerizes by fumarate or maleate double bonds which are randomly distributed in the polyester backbone. Peroxide-cured unsaturated polyesters have been used commercially for many years (5). According to the patent literature (11), UV-curable unsaturated polyesters are quite similar in composition to resins used commercially for peroxide cures. Properly UV-cured unsaturated polyesters have been found to give properties equivalent to peroxide-cured systems. The UV-method therefore has found its first application in the cure of these materials. The process is now used in furniture and cabinet manufacture whiere unsaturated polyesters find use as board fillers, top coats for furniture, doors, panels, panelling etc. (8, 9, 11).

During recent years orthopaedic casts cured by ultraviolet light have been increasingly used. Usually they consist of an unsaturated polyester with vinyl toluene as monomer and a benzoin-ether molecule as photo-initiator. The resin is impregnated into a fiberglass weave.

Suspicion regarding health hazards from inhalation of the monomers, styrene and vinyl toluene, is one of the reasons for developing the second major class of UV-curable polymers consisting of thermoplastic resins into which the reactive acrylate or methacrylate have been introduced.

The reactive acrylate groups are attached to the backbone of the resins through functional groups.

The prepolymers used in UV-curing ink formulations usually are synthetic resins with terminal acrylate groups. The most common are diacrylate esters of polyesters, polyethers, urethanes and epoxy resins. The commercially used UV-curing inks are a mixture of acrylated prepolymer, multifunctional acrylic monomer, photo-initiator and inhibitor.

During recent years, contact allergy has been reported from acrylates used in UV-curing inks (1, 2, 6, 7, 10, 12) and some have been proved to be potent sensitizers (3, 4, 14).

Of the 6 men with dermatitis, when working with

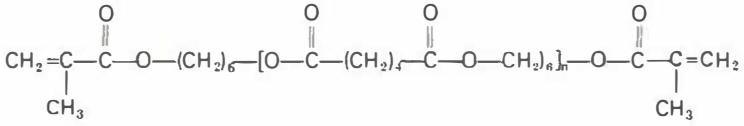

Fig. 1. Methacrylic oligomers based on polyester (methacrylated polyester).

UV-curing inks, discussed in previous investigations (1, 2), 3 reacted to the polyester methacrylate they had been exposed to.

The purpose of this study was to investigate the sensitizing cpacity of the polyester methacrylate present in the ink used, with the "Guinea pig maximization test" (GPM test).

MATERIALS AND METHODS

The methods were principally the same as in previous work (3, 4) and were in accordance with the original description of the GPM test.

Animals. Albino female guinea pigs, weighing 300–400 g, were used. The animals were kept in the pen for a week before the experiments.

Chemicals. The polyester methacrylate used for sensitization and challenge was commercial available (Ebecryl 810, UCB, furnished by Grafisk Färg AB, Stockholm, Sweden) and used in the printing industry (Fig. 1).

Challenge was also performed with methyl methacrylate (MMA) and methylacrylate (MA).

Topical irritancy. The topical irritancy of the chemicals was studied by a 24-hour closed patch test in 6 animals not used in the test. A challenge patch test concentration was used which did not give any reaction.

Sensitization concentrations. Preliminary investigations were performed in 6 animals to establish the optimal sensitization concentration of polyester methacrylate for intradermal and topical induction without causing systemic toxicity.

The final concentration for intradermal induction with polyester-acrylate was 10% in liquid paraffin. For topical induction, 100% concentration was used. Pretreatment with sodium lauryl sulphate gave a too strong reaction.

Challenge. All animals were tested with polyester methacrylate in a concentration of 5% in acetone. Only evident redness and/or swelling was regarded as an allergic response. The reactions were evaluated blind and an assistant chose the cages of the animals at random.

Simultaneously with the challenge with the polyester methacrylate, the animals were also patch tested with MMA and MA, both in a concentration of 2% in acetone.

Controls. At the same time as the animals in the experimental group were sensitized, the control animals were also exposed intradermally to Freund's complete adjuvant (CFA) and vehicle. For the topical induction a dry cotton webril was used. When the sensitized animals were challenged the control animals were also patch tested with the same chemicals and in the same concentrations.

RESULTS

Six (33%) of 20 animals exposed to polyester methacrylate became sensitized. Methyl methacrylate and methylacrylate gave no reactions in the sensitized animals. There were no reactions at all in the control animals to any of the compounds.

The test results are summarized in Table 1.

DISCUSSION

Thirty-three per cent of the guinea pigs were sensitized to polyester methacrylate, which can be classified as a moderate sensitizer.

Fifty per cent of the workers with dermatitis from UV-curing inks in the printing plant earlier discussed (1, 2) had positive test results from polyester methacrylate. The workers had been exposed fairly frequently to polyester methacrylate, a common prepolymer in the inks used.

The polyester methacrylate tested (Ebecryl 810, UCB, Belgium) is, according to the manufacturer, a dimethacrylated polyester, thus a saturated polyester terminated with methacrylic groups.

The unsaturated polyester prepolymer used in conventional UV-curing coatings is typically prepared from maleic anhydride, an aromatic anhydride and a diol and has many double bonds in its molecular structure, which can easily undergo radical changes important in the polymer formation (9).

To my knowledge, no allergic contact dermatitis

Table 1. *Challenge reactions in 20 animals sensitized to polyester methacrylate. Challenge concentrations in acetone*

Animals	Polyester methacrylate 5%	Methyl methacrylate 2%	Methyl-acrylate 2%
Number	6	0	0
Per cent	33	0	0
Controls	0	0	0

caused by unsaturated polyesters has been reported.

Probably, the whole molecular structure of polyester methacrylate acts as an allergen, since none of the animals reacted when tested with methyl methacrylate or methacrylate. However, the reactive terminal methacrylate groups seem to be of great importance for antigen formation and sensitization.

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HLA Antigens in Discoid Lupus Erythematosus

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Abstract. HLA-A, B, C and Bf typing was performed in 55 cases of Discoid Lupus Erythematosus (DLE). When both the sex and age of the patient at the onset of the disease were taken into consideration (group I under 40 years, group II over 40), the following increases in antigen frequency were observed: group I: A2 in women, B5, A10 in men; group II: Aw19.2 in women, B8 in both sexes. Nevertheless, if the probability is multiplied by the number of antigens tested, these results are no longer significant.

Key words: Discoid Lupus Erythematosus; HLA typing

In 1977 Millard et al. (5) investigated 69 cases of Discoid Lupus Erythematosus (DLE). HLA typing showed an increased frequency of HLA-B7, B8 and Bw35 antigens related to the sex of the patient and the age of onset of the disease. In order to compare our results with those of these authors, 55 cases of DLE were studied.

PATIENTS AND METHODS

Fifty-five patients with DLE, 33 men and 22 women, were typed for HLA-A, B, C and Bf antigens. When the age of onset of the disease was studied, the patients could be divided into two groups: (i)—group I with 23 cases, 22 of then aged between 20 and 35 years and 1 case aged 3; (ii)—group II with 32 cases aged between 41 and 67 years.

Classification of patients according to their sex was as follows. Group I: 15 men and 8 women; group II: 18 men and 14 women. Patients were selected as follows (*a*) clinical diagnosis by a dermatologist; (*b*) confirmation by biopsy examined in the same histology laboratory.

The following HLA antigens were investigated HLA-A1, A2, A3, A9, A10, A11, Aw19.2 (Aw30+Aw31), A28, A29, Aw32, Aw33; HLA-B5, B7, B8, B12, B13, B14, B15, Bw16, B17, B18, Bw21, Bw22, B27, Bw35, B37, B40; HLA-Cw2, Cw4, Cw5. Bf phenotyping was performed by