54 Polyester Resins

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Core Messages

- Allergic contact dermatitis from polyester resins is rare.
- Allergic reactions are more likely to occur from other components of the resin system, but are still uncommon. Irritant contact dermatitis may occur from peroxides and styrene.
- Contact urticaria may occur from anhydrides.

1 Introduction

Polyester resins are polycondensates prepared in two different forms: saturated and unsaturated. Saturated polyesters, alkyd resins, are produced from polybasic acids and polyalcohols. Polybasic acids, mainly phthalic acid or maleic acid, are used in their anhydride forms. The polyalcohols most often used are glycerol, pentaerythriol, or trimethylolpropane.

The saturated polyesters, synthesized in this way, are also named unmodified alkyd resins, macromolecules commonly used as plasticizers for other plastic materials. Alkyd resins can be modified by oil-containing fatty acids to be used in water-based paints and surface coatings (Kanerva et al. 1996a; Björkner 2006).

Unsaturated polyester (UP) resins are produced through esterification of dicarboxylic acids or their anhydrides, such as maleic anhydride, phthalic anhydride, or fumaric acid, and diols, such as diethylene glycol or 1,2-propylene glycol (*Fig. 54.1*). Styrene is the most commonly used monomer for the cross-linking of UP resins. Vinyl toluene and methyl methacrylate are examples of other cross-linking agents.

An initiator or catalyst is required to start the cross-linking process, and is usually a peroxide such as benzoyl peroxide or methyl ethyl ketone peroxide. Accelerators, such as cobalt naphthenate or octoate, or tertiary amines such as dimethyl aniline, diethyl aniline, and dimethyl-p-toluidine, are also necessary for the curing of plastics at room temperature. The ultraviolet light (UV)-curable polyester system is used in the furniture industry as top coating and for orthopedic casts. The UV-curable polyester system contains vinyl toluene as the cross-linking agent and a benzoin-ether molecule as photoinitiator (Kanerva et al. 1996a; Björkner 2006). UP resins have been used extensively in the reinforced plastics industry in the manufacture of products for transportation, construction, and marine applications. They are also used for coatings, finishes, lacquers, cements, and glues (Kanerva et al. 1996a; Björkner 2006).

2 Skin Problems from Polyester Resins

Saturated polyester resins are generally not considered to be sensitizing. Allergic contact dermatitis (ACD) has, however, been caused by an epoxy compound, triglycidyl isocyanurate (TGIC) used as cross-linker in polyester paints (Mathias 1988). Phthalic anhydrides have been reported to cause ICD (Malten and Zielhuis 1964), immediate IgE-mediated hypersensitivity with asthma, allergic rhinitis, urticaria (Jolanki et al. 1987, 1997; Tarvainen et al. 1995a) and, rarely, ACD (Kanerva et al. 1997). The contact urticaria reaction from methyl hexahydrophthalic anhydride was reported to be enhanced by wiping off the substance with an alcohol disinfectant, which was presumed to enhance penetration of the allergen (Kanerva et al. 1999a).

Most reports of skin problems involve workers in plastics manufacture. In one workplace study (Minamoto et al. 2002a), ACD was most common but irritant contact dermatitis (ICD) was also reported, from both chemicals and mechanical irritants such as glass fiber and dust. As manufacturing processes become increasingly automated, exposure to alkyd resins is generally a result of accidents or maintenance work.

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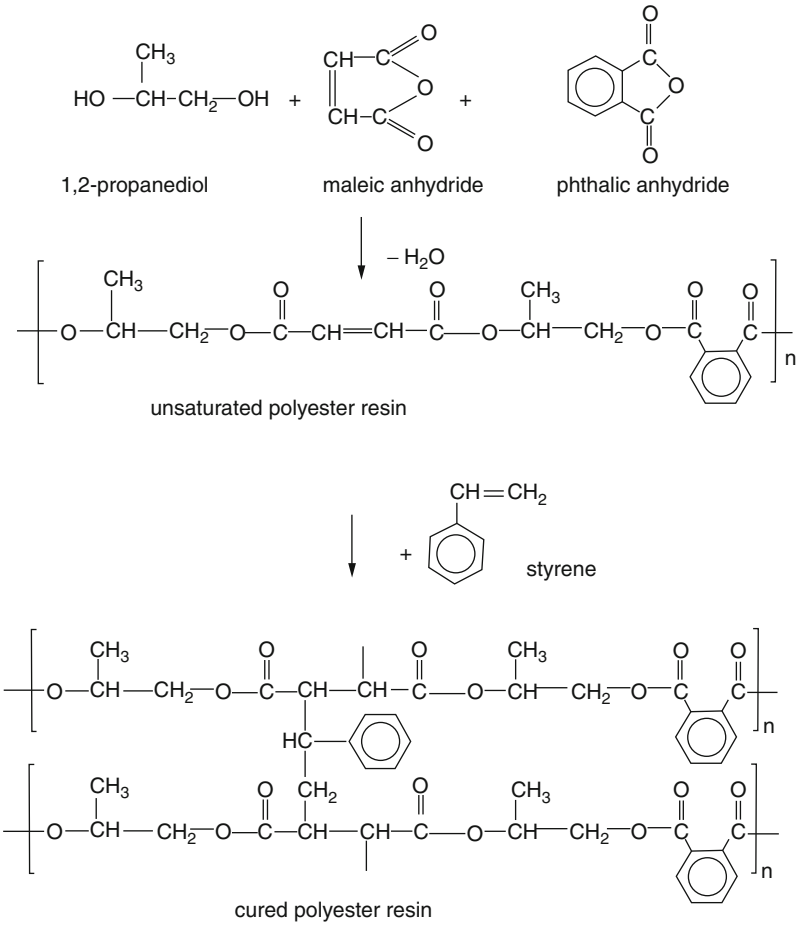

Fig. 54.1
Unsaturated polyester resin is made by condensing 1,2-propanediol, maleic anhdyride, and phthalic anhydrides. Styrene is used as a cross-linking monomer

3 Irritant Contact Dermatitis

ICD from UP resins occurs from cross-linking styrene (Rietschel and Fowler 2008) or, in earlier times, diallylphthalate (Fregert 1971). Styrene is classified as a mild irritant, although it has been reported to cause blisters (Bourne and Milner 1963) and even chemical burns (Bruze et al. 2000).

Prolonged exposure to styrene has caused a case of skin atrophy, neurogenic muscular atrophy, and anxiety reaction (Araki et al. 1971). Levels of styrene vapor exceeding 300 ppm (1,260 mg/m) have been reported to induce erythema of the skin (Stewart et al. 1968). Even at levels of 50 ppm (215 mg/m), styrene vapor may irritate conjunctival and nasal mucous membranes (Gotell et al. 1972). The mucous membrane irritation may be caused by the vinyl group in styrene (Alarie 1973). However, workers may develop a tolerance to the irritation after prolonged exposure (Gotell et al. 1972).

Organic peroxides, used as 3–10% solutions to catalyze the hardening reactions of UP, are weak sensitizers but strong irritants (Haustein et al. 1985). In the plastic composite industry, organic peroxides have caused severe ICD (Bourne and Milner 1963). Reactive organic peroxide molecules in unhardened resin dust may cause stinging on uncovered areas of the skin during spray lamination (Schumes 1990).

Hydrogen peroxide is an irritant but very rarely an allergen (Aguirre et al. 1994; Kanerva et al. 1998). Phthalic anhydride used in the manufacture of alkyd resins can cause ICD, and even caustic blisters especially on moist skin, where the anhydride is transformed into the corresponding acid (Malten and Zielhuis 1964).

In addition to chemicals included in the resin system, mold-releasing chemicals have also caused ICD (Bourne and Milner 1963). Acetone is used to clean equipment in UP resin industries. With repeated contact, acetone may defat the skin and disrupt the epidermal barrier (Fartasch 1997). It has been reported to be a contributing factor for ICD in this industry (Bourne and Milner 1963; Tarvainen et al. 1993b, 1994). Chlorinated hydrocarbon solvents such as methylene chloride and trichloroethane are often used for cleaning purposes and are also skin irritants (Midtgard and Knudsen 1994).

4 Allergic Contact Dermatitis

ACD was first reported from UP resins in 1955 (Lieber 1955). Five patients with ACD and positive patch tests to UP resins were reported from a group of 30 workers in an airplane factory (Malten 1956). Most cases of ACD have been caused by exposure to UP resin in lamination work (Malten 1956; Bourne and Milner 1963; Lidén et al. 1984), in painting (Kadlec et al. 1974), or in the use of UV light-cured inks (Björkner 1982).

UP dust from reinforced plastic products (Bourne and Milner 1963; Tarvainen et al. 1993b, 1995b) or UP automobile-repair putty (Tarvainen et al. 1993a; Kanerva et al. 1999b; Dooms-Goossens and De Jonge 1985) have also caused ACD.Guin (2001) reported a machine repairman who had developed ACD from adipic acid while working in the synthesis of polyester resins.

Adipic polyester, produced from adipic acid and propylene glycol, is a thermoplastic polyester used as a plasticizer in vinyl gloves, and has also caused ACD (Sowa et al. 2005). Nonoccupational ACD from UP resin is infrequent, but has been reported from "hypoallergenic" nail varnish (Shaw 1989), UP glue (Sjoborg et al. 1982), and limb prostheses (MacFarlane et al. 1986; Freeman 1986; Vincenzi et al. 1991; Haddad et al. 1996).

The allergens are often the auxiliary chemicals used, such as cobalt naphthenate (Key et al. 1961; Bourne and Milner 1963; Malten and Zielhuis 1964; Kadlec et al. 1974), cobalt octoate (cobalt-2-ethylhexanoate) (Kanerva et al. 1996b) and more recently in a spa bath laminator (Anavekar and Nixon 2006); dibutyl phthalate, dimethyl phthalate, dioctyl phthalate (Malten and Zielhuis 1964), tricresyl phosphate (Key et al. 1961), or a cross-linking monomer, such as styrene (Key et al. 1961; Bourne and Milner 1963; Sjoborg et al. 1982; Conde-Salazar et al. 1989), or a catalyst such as benzoyl peroxide (Bourne and Milner 1963; Malten and Zielhuis 1964;

Table 54.1
Allergens in unsaturated polyester (UP) resins

Actual allergen in UP resin	
Maleic acid	Malten and Zielhuis (1964)
Fumaric acid	Malten and Zielhuis (1964)
Adipic acid	Malten and Zielhuis (1964), Guin (2001)
Phthalic anhydride	Malten and Zielhuis (1964), Lidén et al. (1984)
Maleic anhydride	Minamoto et al. (2002b)
Maleic esters	Minamoto et al. (2002b), Malten (1984)
Polyester methacrylate	Björkner (1982)
Methyl methacrylate	Wehle (1966)
Diethylene glycol maleate	Tarvainen et al. (1993a), Kanerva et al. (1999b); Pfaffli et al. (2002)
Cross-linking monomers	
Styrene	Key et al. (1961), Bourne and Milner (1963), Sjoborg et al. (1982), Conde-Salazar et al. (1989)
Vinyltoluene	Sjoborg et al. (1982)
Hardening catalysts	
Benzoyl peroxide	Bourne and Milner (1963), Vincenzi et al. (1991)
Cyclohexanone hydroperoxide	Malten (1964)
Methyl ethyl ketone peroxide	Bourne and Milner (1963), Malten and Zielhuis (1964)
Cobalt salts	Kanerva et al. (1996b), Minamoto et al. (2002)
Cobalt naphthenate	Key et al. (1961), Bourne and Milner (1963), Malten and Zielhuis (1964), Kadlec et al. (1974)
Cobalt octoate	Anavekar and Nixon (2006)
Inhibitor	
Hydroquinone	Torres et al. (1993)
p-tert-Butyl catechol (in styrene)	Estlander et al. (1998)
Artificial limbs (made of UP resin)	
p-tert-Butyl catechol	MacFarlane et al. (1986), Freeman (1986)
Benzoyl peroxide	Vincenzi et al. (1991)
Dimethyl-p-toluidine	Haddad et al. (1996)
Others	
Pthalates	Malten and Zielhuis (1964)
Tricresyl phosphate	Key et al. (1961)

Table 54.2
Allergic and nonallergic (negative) patch-test reactions to the components of polyester resin (Kanerva et al. 1999b, Pfaffli et al. 2002)

Allergic patch-test reaction to:	Negative patch-test reaction to:
Patient's own two-component polyester cement (sanding dust)	Hardener component (including benzoyl peroxide) (1%)
Resin component (UP resin in styrene with auxiliary substances and filling materials) (1–10%)	Filling materials (100%)
UP resin in styrene with auxiliary substances (10%)	Styrene (1%)
Pure UP resin in styrene (2.5% in acetone)	Auxiliary substances (1%)
Purification: TLC bands found at Rf-value of 0.24 ± 0.03 (*n* = 6) (100%)	Ingredients of UP resin
Identification: Diethylene glycol maleate (MW 204) (0.1–0.01%)	

TLC thin-layer chromatography, *MW* molecular weight (in kilodaltons), *Rf* retention factor

Vincenzi et al. 1991), cyclohexanone hydroperoxide (Malten 1964), or methyl ethyl ketone hydroperoxide (Bourne and Milner 1963; Malten and Zielhuis 1964). Lymphomatoid-like contact dermatitis in a marble worker was reported from cobalt naphthenate (Schena et al. 1995).

The allergens have been summarized in *Table 54.1*. Eight patients were reported to be allergic to UP resins from car-repair painting and mold manufacturing (Tarvainen et al. 1993a; Kanerva et al. 1999b).

A patch testing strategy was developed by Kanerva's group in order to clarify the allergic components of UP resins and has been summarized in *Table 54.2*. All patients reacted on patch testing to the UP resin component of a cement they had used in their work.

Five patients also reacted to hardened UP resin cements, indicating that the hardened UP resin contains reactive monomers. Grinding the resin can give airborne allergic reactions many years after it has been hardened (Kanerva et al. 1999b). The causative allergen was found to be diethylene glycol maleate (DEGM) (Tarvainen et al. 1993a; Kanerva et al. 1999b; Pfaffli et al. 2002).

In another workplace study, ACD was caused not only by UP resin, but by cobalt, benzoyl peroxide, methyl ethyl ketone peroxide, para-tertiary butyl catechol, styrene, and formaldehyde (Minamoto et al. 2002b).

UP resins have been patch tested at concentrations of 0.5–10% (Tarvainen et al. 1993a; Kanerva et al. 1999b) but also at 20% in acetone (Foussereau et al. 1982). In one patient, a concentration of 1% caused a weak allergic reaction (Tarvainen et al. 1993a), and it was suggested that the test concentration may need to be as high as 5% (Kanerva et al. 1999b). However, it is not clear at what concentration active sensitization may occur.

References

Aguirre A, Zabala R, Sanz de Galdeano C, Landa N, Diaz-Perez JL (1994) Positive patch tests to hydrogen peroxide in 2 cases. Contact Dermatitis 30:113

Alarie Y (1973) Sensory irritation of the upper airways by airborne chemicals. Toxicol Appl Pharmacol 24:279–297

Anavekar A, Nixon R (2006) Occupational allergic contact dermatitis to cobalt octoate included as an accelerator in polyester resin. Australas J Dermatol 47:143–144

Araki S, Abe A, Vshio K, Fujino M (1971) A case of skin atrophy, neurogenic muscular atrophy and anxiety reaction following long exposure to styrene. Jpn J Ind Health 13:427–431

Björkner B (1982) Sensitizing capacity of polyester methacrylate in ultraviolet curing inks tested in the Guinea pig. Acta Derm Venereol 62:153–182

Björkner B (2006) Other Plastics 34.5. In: Frosch PJ, Menné T, Lepoittevin J-P (eds) Contact dermatitis. Springer, Berlin/Heidelberg/New York, pp 607–608

Bourne L, Milner F (1963) Polyester resin hazards. Br J Ind Med 20: 100–109

Bruze M, Fregert S, Gruvberger B (2000) Chemical skin burn. In: Menné T, Maibach HI (eds) Hand eczema. CRC Press, Boca Raton, pp 117–125

Conde-Salazar L, Gonzales M, Guimaraens D, Romero L (1989) Occupational allergic contact dermatitis from styrene. Contact Dermatitis 21:112

Dooms-Goossens A, De Jonge G (1985) Contact allergy to unsaturated polyester in a boat builder. Contact Dermatitis 12:238

Estlander T, Kostiainen M, Jolanki R, Kanerva L (1998) Active sensitization and occupational allergic contact dermatitis caused by para-tertiary-butylcatechol. Contact Dermatitis 38:96–100

Fartasch M (1997) Ultrastructure of the epidermal barrier after irritation. Microsc Res Tech 37:193–199

Foussereau J, Benezra C, Maibach HI, Hjorth N (1982) Occupational contact dermatitis. Clinical and chemical aspects. Munksgaard, Copenhagen

Freeman S (1986) Contact dermatitis of a limb stump caused by p-tertiary butyl catechol in the artificial limb. Contact Dermatitis 14:68–69

Fregert S (1971) Outbreak of irritant contact dermatitis from diallylphthalate in polyester resin. Contact Dermatitis Newslett 10:234

Gotell P, Axelson O, Lindelof B (1972) Field studies on human styrene exposure. Work Environ Health 9:76–83

Guin JD (2001) Sensitivity to adipic acid used in polyester synthesis. Contact Dermatitis 44:256–257

Haddad FS, Cobb AG, Bentley G, Levell NJ, Dowd PM (1996) Hypersensitivity in aseptic loosening of total hip replacements. The role of constituents of bone cement. J Bone Joint Surg Br 78:546–549

Haustein V-F, Tegetmeyer L, Ziegler V (1985) Allergic and irritant potential of benzoyl peroxide. Contact Dermatitis 13:252–257

Jolanki R, Estlander T, Kanerva L (1987) Occupational contact dermatitis and contact urticaria caused by epoxy resins. Acta Derm Venereol Suppl (Stockh) 134:90–94

Jolanki R, Kanerva L, Estlander T, Tarvainen K (1997) Skin allergy caused by organic acid anhydrides. In: Amin S, Lahti A, Maibach HI (eds) Contact urticaria syndrome. CRC Press, Boca Raton, pp 217–224

Kadlec K, Hanslian L, Forprechtová A (1974) Occurrence of skin disease as a result of work with polyester varnishes (in Czech). Cesk Dermatol 49:281–289

Kanerva L, Björkner B, Estlander T, Jolanki R, Tarvainen K (1996a) Plastic materials: occupational exposure, skin irritancy and its prevention. In: van der Valk P, Maibach HI (eds) The irritant contact dermatitis syndrome. CRC Press, Boca Raton, pp 127–155

Kanerva L, Jolanki R, Estlander T (1996b) Offset printer's occupational allergic contact dermatitis caused by cobalt-2-ethylhexoate. Contact Dermatitis 34:67–68

Kanerva L, Hyry H, Jolanki R, Hytonen M, Estlander T (1997) Delayed and immediate occupational allergy caused by methylhexahydrophthalic anhydride. Contact Dermatitis 36:34–38

Kanerva L, Jolanki R, Riihimäki V, Kalimo K (1998) Patch test reactions and occupational dermatoses caused by hydrogen peroxide. Contact Dermatitis 39:146

Kanerva L, Alanko K, Jolanki R, Estlander T (1999a) Airborne allergic contact urticaria from methyl hexahydrophthalic anhydride and hexahydrophthalic anhydride. Contact Dermatitis 41:339–341

Kanerva L, Estlander T, Alanko K, Pfäffli P, Jolanki R (1999b) Occupational allergic contact dermatitis from unsaturated polyester resin an a car repair putty. Int J Dermatol 38:447–452

Key MM, Perone VB, Birmingham DJ (1961) Patch testing in dermatitis from the newer resins. J Occup Med 3:361–364

Lidén C, Löfström A, Storgårds-Hatam K (1984) Contact allergy to unsaturated polyester in a boat builder. Contact Dermatitis 11: 262–264

Lieber EE (1955) Dermatitis – an industrial problem. Br Plastics 28: 428–429

MacFarlane AW, Curley RK, King CM (1986) Contact sensitivity to unsaturated polyester resin in a limb prosthesis. Contact Dermatitis 15:301–303

Malten KE (1956) Occupational eczema in processing plastics (doctoral dissertation in Dutch with English summary). University of Amsterdam, Amsterdam

Malten KE (1964) Einige Bemerkungen zur Hautsensibilisierung durch Aethoxylin {Epoxyd)-Kunstharze und deren Prophylaxe. Derm Beruf Umwelt 2:78–85

Malten KE, Zielhuis R (1964) Polyester resins. In: Malten KE, Zielhuis R (eds) Industrial toxicology and dermatology in the production and processing of plastics. Elsevier, Amsterdam, pp 71–84

Malten KE (1984) Dermatological problems with synthetic resins and plastics in glues. Part 11. Derm Beruf Umwelt 32:81–86

Mathias CGT (1988) Allergic contact dermatitis from triglycidyl isocyanurate in polyester paint pigments. Contact Dermatitis 19: 67–68

Midtgard U, Knudsen LE (1994) Fibre-reinforced plastics and advanced polymer composites. Occupational hazards and toxicity of selected compounds.. Nordic Council of Ministers and National Institute of Occupational Health, Copenhagen, pp 1–73

Minamoto K, Nagano M, Inaoka T, Futatsuka M (2002a) Occupational dermatoses among fiberglass-reinforced plastics factory workers. Contact Dermatitis 46:339–347

Minamoto K, Nagano M, Yonemitsu K, Futatsuka M (2002b) Allergic contact dermatitis from unsaturated polyester resin consisting of maleic anhydride, phthalic anhydride, ethylene glycol and dicyclopentadiene. Contact Dermatitis 46:62–63

Pfaffli P, Jolanki R, Estlander T, Tarvainen K, Kanerva L (2002) Identification of sensitizing diethyleneglycol maleate in a two-component polyester cement. Contact Dermatitis 46:170–173

Rietschel RL, Fowler JF Jr (2008) Fisher's contact dermatitis, 6th edn. McGraw-Hill, New York

Schena D, Rosina P, Chieregato C, Colombari R (1995) Lymphomatoid-like contact dermatitis from cobalt napthenate. Contact Dermatitis 33:197–198

Schumes E (1990) Solvents and plastizers. In: Adams RM (ed) Occupational skin disease, 2nd edn. WB Saunders, Philadelphia

Shaw S (1989) A case of contact dermatitis from "hypoallergenic" nail varnish. Contact Dermatitis 20:385

Sjoborg S, Dahlquist I, Fregert S, Trulson L (1982) Contact allergy to styrene with cross reaction to vinyltoluene. Contact Dermatitis 8:207–208

Sowa J, Kobayashi H, Tsuruta D et al (2005) Allergic contact dermatitis due to adipic polyester in vinyl chloride gloves. Contact Dermatitis 53:243–244

Stewart RD, Dodd HC, Baretta ED, Schaffer AW (1968) Human exposure to styrene vapor. Arch Environ Health 16:656–662

Tarvainen K, Jolanki R, Estlander T (1993a) Occupational contact allergy to unsaturated polyester resin cements. Contact Dermatitis 28: 220–224

Tarvainen K, Jolanki R, Forsman-Gronholm L, Estlander T, Pfaffli P, Juntunen J, Kanerva L (1993b) Exposure, skin protection and occupational skin diseases in the glass-fibre reinforced plastics industry. Contact Dermatitis 29:119–127

Tarvainen K, Estlander T, Jolanki R, Kanerva L (1994) Occupational dermatoses caused by man-made mineral fibers. Am J Contact Dermat 5:22–29

Tarvainen K, Jolanki R, Estlander T, Tupasela O, Pfaffli P, Kanerva L (1995a) Immunologic contact urticaria due to airborne methylhexahydrophthalic and methyl tetrahydrophthalic anhydrides. Contact Dermatitis 32:204–209

Tarvainen K, Kanerva L, Jolanki R, Estlander T (1995b) Occupational dermatoses from the manufacture of plastic composite products. Am J Contact Dermat 6:95–104

Torres V, Mano-Azul AC, Correia T, Soares AP (1993) Allergic contact cheilitis and stomatitis from hydroquinone in an acrylic dental prosthesis. Contact Dermatitis 29:102–193

Vincenzi C, Cameli N, Vassilopoulou A, Tosti A (1991) Allergic contact dermatitis due to benzoyl peroxide in an arm prosthesis. Contact Dermatitis 24:66–67

Wehle U (1966) Arbeitsbedingte Ekzeme durch Polyester. Allerg Asthma (Leipz) 12:184–186